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Occurrence of Pharmaceutical Compounds in Groundwater from the Gran Canaria Island (Spain)

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Abstract: The presence of pharmaceutical compounds in the whole environment is a growing concern. These compounds might be present in the effluents of wastewater treatment plants and, hence, irrigation with treated sewage may be a source of groundwater pollution. The volcanic aquifer that lies NE of Gran Canaria (Spain) was studied to address the relationship of the occurrence of pharmaceutical compounds and a golf course that has been irrigated with regenerated water since 1973. Of the 14 analyzed groundwater samples, five wells were chosen to perform annual monitoring. Irrigation water and soil leachate were also evaluated. The target analytes were atenolol, metamizole, fluoxetine, ibuprofen, nicotine, permethrin, caffeine, and their metabolite paraxanthine. The environmental risk is limited as the concentrations of the pharmaceuticals measured in the sampled wells were always below 60 ng·L^{-1} (lower than the detected caffeine and nicotine concentrations). Wide variations for the same wells were measured among sampling campaigns, and also among the different wells. The study points to the importance of sample conservation during transport and the need to perform analyses immediately, or to follow an in-situ extraction procedure to carry concentrated samples under better conditions.

Keywords: emerging contaminants; volcanic aquifer; reclaimed water reuse; irrigation; Gran Canaria

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1. Introduction

Pharmaceutical compounds are widely used for many purposes in our modern society, and often with no medical prescription. They belong to the large family of emerging compounds, the majority of which are neither subjected to regulation nor included in monitoring programs. However, it has been demonstrated that they have effects on organisms, such as behavior and reproduction [1].

Once excreted, they enter wastewater treatment plants (WWTPs), which do not possess specific mechanisms to completely eliminate them. Therefore, treated waters have a typically strong contaminating effect on natural aquatic systems, as far as emerging pollutants are concerned [2].

However, pharmaceutical compounds can reach aquifers by not only urban or hospital effluents, but also by reclaimed water used for irrigation, leaks in septic tanks, livestock, or agricultural activities [3]. Then they can undergo several processes on their way to aquifers, such as adsorption, ion exchange, and microbial degradation or transformations [4]. In volcanic materials, the presence of preferential paths in the unsaturated zone can favor rapid recharge through fractures, and contaminants can reach aquifers in relatively short times [5]. Other processes, such as dilution, adsorption, and degradation, can also alter pollutants inside aquifers, which depends on several factors related to geological material and climate conditions.

As it offers a guaranteed supply for agriculture, the use of reclaimed water for irrigation is indicated in areas with scarce water resources [6–8]. Gran Canaria (Canary Islands, Spain) is an example of such use, which has been a practice for more than 40 years to irrigate a golf course [9], and also for agriculture. This water can even be used to recharge aquifers [10] or for ecological services, as regulated by Spanish legislation [11]. Despite the removal and dissipation of some emerging pollutants possibly attributing to natural attenuation processes (e.g., sorption into soil, photodegradation, biodegradation), the control of these phenomena and the understanding of transport mechanisms are essential [12].

The presence of pharmaceutical compounds in groundwater in relation to the use of reclaimed waters has been already proven in places where raw water is reused; in Germany, England, France, and Mexico, infiltration of untreated municipal wastewater was employed in the late 19th century, and, although this practice no longer continues, pollutants may still be present in soil and groundwater [13].

On pharmaceutical compounds, several studies have demonstrated the correlation between using reclaimed water and its presence in groundwater. Thus, a long list of different drugs, such as antibiotics, anti-inflammatories, stimulants, β-blockers, analgesics, or antidepressants, has been measured in several aquifers [14–19]. Nevertheless, information about emerging contaminants in volcanic aquifers is scarce in other areas outside the Gran Canaria Island [5,9]. Moreau et al. [20] and Close et al. [21] checked the existence of pharmaceuticals and other emerging contaminants in New Zealand, where volcanic aquifers are present. No references to the aquifer nature are included in Close et al. [21], while Moreau et al. [20] point out the existence of pharmaceuticals among other emerging contaminants in ignimbrites, basalts, and confined pumice and unconfined aquifers, but no specific behavior for pharmaceuticals in these aquifers has been identified.

In this work, the study of different pharmaceutical residues in a volcanic aquifer on the Gran Canaria Island was carried out to assess their occurrence in groundwater, the origin of contamination, and possible transport mechanisms. Irrigation water from a golf course irrigated with reclaimed water and soil leachate from a lysimeter were also evaluated to compare the results.

2. Materials and Methods

2.1. Study Area

The Gran Canaria Island is conceptually considered a unique water body, save for the coastal part of the west catchment [22,23]. The study area is located northeast of the island (Figure 1) and includes the Las Goteras ravine watershed where the Bandama golf course is located at an altitude of between 400 m and 500 m. The geological materials that outcrop in the golf course area are Holocene basaltic lava and pyroclastics (2000 years old) from the volcanic eruptions that formed the Caldera de Bandama [24]. They are placed on the fractured Pliocene basanitic lava flows and landslides (Roque Nublo Group) that overlie Pliocene phonolites (Figure 1). Post-Roque Nublo volcanic materials and sedimentary rocks from the Las Palmas Detritic Formation outcrop in the rest of the study area. The water table potentiometric map shows that groundwater flows from the summit of the island to the coast. In the area, preferential paths have been identified through the Las Goteras ravine and from the golf course to the Las Goteras Ravine. Cultivated soils are Torriarents (adjacent natural soils are Vitritorrands) and the golf course has also transported soil from the midlands, corresponding to an Ustalfs-dominated zone. The average precipitation in the area is 300 mm per year, with an average annual temperature of 19 °C, while the minimum humidity in winter and the maximum humidity in summer are 78% and 85%, respectively [25].

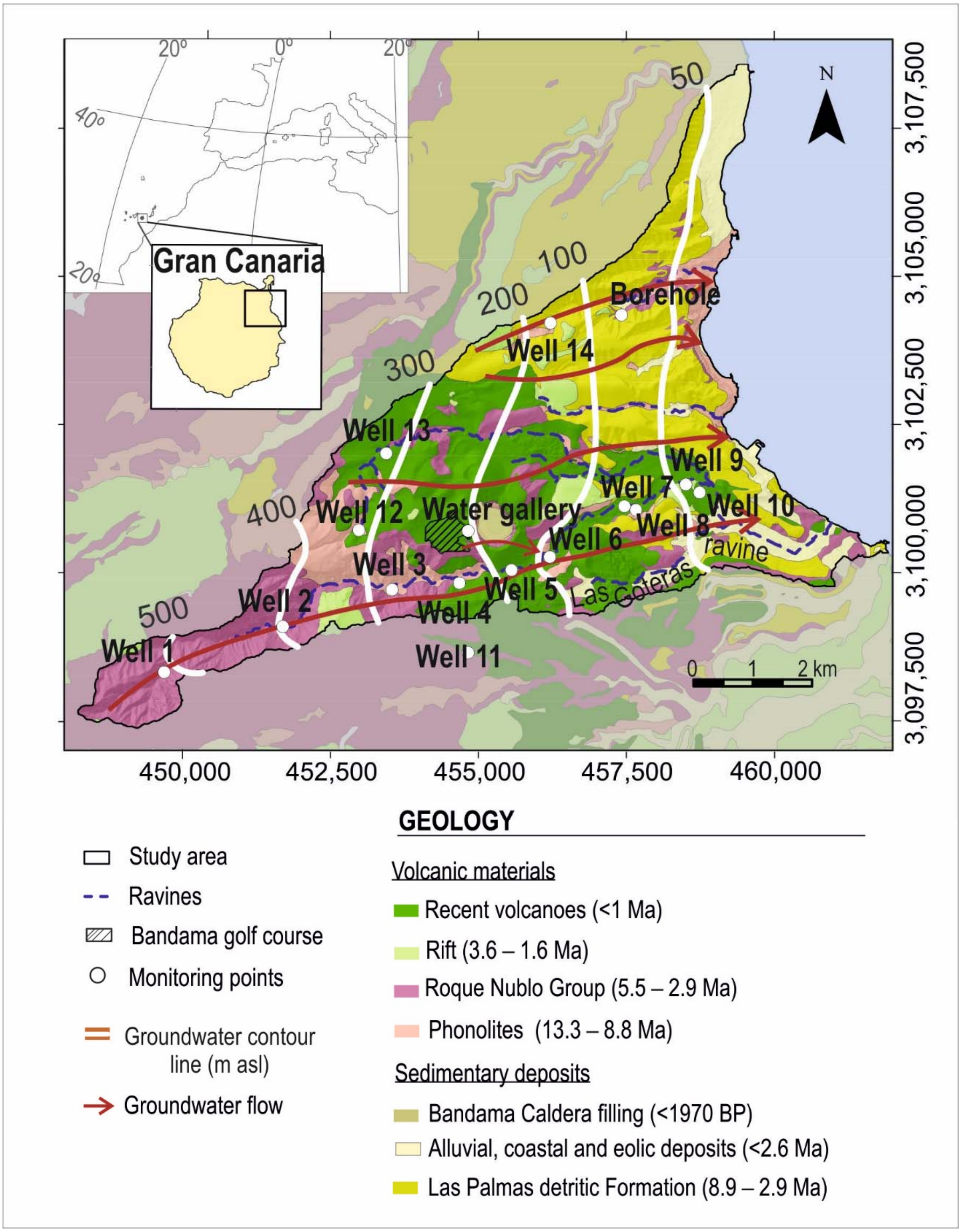

Figure 1. Location and geology of the study area. Ravines situation, Bandama Caldera, Bandama Golf Course and potentiometric water table lines for the 2008 data are shown. Monitoring points include Canarian wells, the El Culatón water gallery, and the borehole.

A first detailed field survey was carried out in 2008 to know the state of the groundwater works in the area and hydrogeological features. From these data, the potentiometric map was drawn (Figure 1), and shows that the groundwater table was located 250 m below the golf course and more than 100 m below the caldera bottom.

Active groundwater works were identified in the area to be sampled (Figure 1). Groundwater is mostly exploited by large-diameter shaft wells (traditional Canarian wells) at most sampling sites, with diameters from 2.5 m to 3 m and depths from 15 m to 300 m. These 13 sampled wells mean that daily yields are less than 1 L s^{-1} and come from different geological formations, depending on well depth. A 0.33-m-diameter borehole and a water gallery of about 40-m-long, located under the wall of the Bandama Caldera, 60 m above the Bandama Golf Course, have also been sampled. This gallery drains a perched aquifer formed by a clay unit from Roque Nublo breccias formed by a landslide. The gallery yield is 0.05 L s^{-1}, and it collects irrigation returns from the Bandama Golf Course as its composition differs from the groundwater sampled at the bottom of the ravine [26]. The groundwater in the study area is used mainly for irrigation purposes.

As indicated in [5], groundwater salinity increases towards the coast, and well 1 is of a sodium bicarbonate type with low mineralization. Towards the coast, groundwater changes to a sodium chloride type, and nitrate contents rise due to progressive mineralization through the flow direction and the influence of saline recharge water due to aridity in coastal areas, as well as anthropogenic activities. Well 6 is of a sodium bicarbonate type with significantly higher Na^+ contents, a low pH, and high HCO^{3-} contents, which indicate that at this point the aquifer is enriched with endogenous CO_2 gas contributions, and this well more deeply exploits the aquifer.

2.2. Sampling Methodology

All the samples from the preliminary campaign were taken between November 2008 and February 2009, including the golf course irrigation water (both from a pond and directly from a sprinkler). The soil leachate from a lysimeter installed in the golf course was taken when available water allowed recovery of water. Groundwater was sampled from the water gallery (two samples), the borehole, and 13 wells. The groundwater from wells and the borehole was sampled after waiting at least 15 min to obtain representative samples from the aquifer.

After studying the preliminary results, longer sampling was designed in an attempt to identify seasonal variation in 2009. The water used for irrigation and from the soil leachate, the water gallery, and five wells were selected to complete a wider study by taking samples quarterly per year.

Samples were taken in 1-litre amber glass bottles with Teflon caps, maintained immediately in cold, and analyzed within the next 48 h in the Analytical Chemistry Laboratory at the University of Las Palmas de Gran Canaria (Spain).

2.3. Reagents, Instrumentation, and Analytical Procedure

The selected analytes were atenolol (β-blocker), metamizole (analgesic), fluoxetine (antidepressant), ibuprofen (anti-inflammatory), nicotine (psycho-active drug), permethrin (antiparasitic), caffeine (stimulant), and their metabolite paraxanthine. They were obtained from Sigma-Aldrich (Madrid, Spain). Stock solutions (1000 mg·mL^{-1}) were prepared in methanol and stored in glass-stoppered bottles at 4 °C prior to use.

The solid-phase extraction procedure (SPE) was employed prior to determining by liquid chromatography–electrospray ionization tandem mass spectrometry (HPLC–ESI–MS/MS) before isolating and preconcentrating the target analytes from samples. All the parameters that affected the extraction and elution of compounds were studied and optimized to obtain the maximum extraction yields. The optimum conditions for extracting the selected pharmaceuticals were the following: Oasis Hydrophilic-Lipophilic Balance cartridge (HLB), 200 mL of sample at pH 8, flow pass at 10 mL·min^{-1}. For the elution, 2 mL of methanol passing at 10 mL·min^{-1} were employed to obtain a preconcentration factor of 100.

Then, a Varian 320-MS triple quadrupole system, equipped with an electrospray ionization (ESI) interface, was employed to identify and quantify compounds. The detection conditions for each compound, established by direct infusion of pure standard, are shown in the Supplementary Material (Table S1). For chromatographic separation purposes, a Waters Sunfire C18 3.0 × 100 mm (3.5 µm particle size) stationary phase and a mobile phase consisting of methanol and water with 0.2% (*v*/*v*) formic acid and 5 mM of ammonium formate were used. The flow rate was 0.2 mL/min and the sample volume injected was 10 µl. LC–MS-grade methanol, LC–MS grade water, formic acid, and ammonium formate were obtained from Panreac Química (Barcelona, Spain), while 200-mg Oasis HLB cartridges were obtained from Waters (Madrid, Spain).

Having optimized the extraction, separation, and detection procedure, the figures of merit (linearity, precision, limits of detection/quantification) were calculated (Supplementary Material, Table S2) to validate the determination of the target pharmaceuticals in the water samples. The external calibration curves within the 1–500 ng·L^{-1} range offered higher linear correlation coefficients than 0.995 for all the target compounds. To evaluate precision, six replicates were performed. The obtained values, expressed as relative standard deviation (RSD, %), ranged from 4.4 to 16.1%. Limits of detection (LODs) and limits of quantification (LOQs) were obtained from the signal and noise ratio (S/N) corresponding to the lowest concentration of the calibration curve by assuming the minimum detectable S/N levels of 3 and 10, respectively. The LODs and LOQs fell within the 2.9–39.4 to 9.5–131.2 ng·L^{-1} range, respectively.

3. Results

3.1. Initial Sampling Campaign Results

In the preliminary field survey, 14 wells, the water gallery, and a borehole (Figure 1) were sampled. The golf course irrigation water, taken from the pond and directly from a sprinkler, as well as the water from a lysimeter (soil leachate), were also analyzed. The results are shown in Table 1.

Table 1. Occurrence of target analytes (ng·L^{-1}) during the initial sampling campaign (nd: not detected).

	Nicotine	Atenolol	Metamizole	Paraxanthine	Caffeine	Fluoxetine
Irrigation water (sprinkler)	132.6 ± 9.0	208.7 ± 17.6	nd	158.0 ± 13.3	116.1 ± 6.8	126.7 ± 16.1
Irrigation water (pond)	102.0 ± 6.9	57.0 ± 4.8	nd	45.4 ± 3.8	38.1 ± 2.2	35.7 ± 4.5
Lysimeter water	180.3 ± 12.3	nd	nd	153.9 ± 12.9	167.0 ± 9.9	28.8 ± 3.7
Gallery (Autumn)	68.7 ± 4.7	6.9 ± 0.6	nd	39.9 ± 3.4	21.8 ± 1.3	nd
Gallery (Winter)	32.3 ± 2.2	8.2 ± 0.7	nd	11.8 ± 1.0	10.4 ± 0.6	nd
Borehole	71.5 ± 4.9	34.8 ± 2.9	nd	193.0 ± 16.2	36.7 ± 2.2	21.5 ± 2.7
Well 1	45.0 ± 3.1	nd	nd	40.1 ± 3.4	29.9 ± 1.8	nd
Well 2	36.7 ± 2.5	nd	3.3 ± 0.1	nd	nd	nd
Well 3	23.2 ± 1.6	nd	nd	nd	19.6 ± 1.2	nd
Well 4	nd	4.3 ± 0.4	nd	13.5 ± 1.1	37.7 ± 2.2	nd
Well 5	nd	nd	nd	nd	nd	nd
Well 6	43.5 ± 3.0	23.6 ± 2.0	nd	65.3 ± 5.5	3.3 ± 0.2	nd
Well 7	73.9 ± 5.0	nd	nd	33.9 ± 2.9	35.7 ± 2.1	nd
Well 8	58.1 ± 4.0	18.4 ± 1.6	16.0 ± 0.7	49.4 ± 4.2	26.4 ± 1.6	47.2 ± 6.0
Well 9	113.6 ± 7.7	21.4 ± 1.8	33.3 ± 1.5	89.5 ± 7.5	14.1 ± 0.8	34.1 ± 4.3
Well 10	111.9 ± 7.6	67.7 ± 5.7	15.1 ± 0.7	22.3 ± 1.9	44.9 ± 2.6	59.2 ± 7.5
Well 11	108.7 ± 7.4	9.1 ± 0.8	nd	144.2 ± 12.1	38.3 ± 2.3	nd
Well 12	40.8 ± 2.8	nd	nd	nd	nd	nd
Well 13	110.6 ± 7.5	38.1 ± 3.2	nd	146.6 ± 12.3	39.2 ± 2.3	nd
Well 14	35.5 ± 2.4	nd	nd	nd	nd	nd

All the studied analytes were detected in wells at concentrations ranging from 3.3 to 146.6 ng·L^{-1}. The irrigation water sampled directly from the sprinkler and in the stored pond showed high concentrations of the target compounds, except for metamizole. Four of the target analytes were found in the lysimeter sample, most at relevant concentrations (nicotine at 180.3 ng·L^{-1}, paraxanthine at 153.9 ng·L^{-1}, and caffeine at 167.0 ng·L^{-1}).

3.2. The 1-Year Monitoring Results

Five wells located in the Las Goteras ravine were selected to form a 1-year monitoring network. This selection was made by mainly attending to their relation to the groundwater flow line through the ravine, which seems to recover water from golf course irrigation. The results of the pharmaceutical contaminants in groundwater, analyzed during the first sampling campaign, were also considered. Wells 9 and 10 showed the highest concentrations during the initial sampling campaign. These wells were not included in the network because they were considered to receive contaminants from other additional sources, and the irrigation returns of the golf course were not the main source. The irrigation water from the sprinkler and the water from the lysimeter were also monitored. Samples were taken every 3 months, and the obtained results are shown in Table 2.

Table 2. Seasonal occurrence of the target analytes (ng·L^{-1}) in the selected samples (nd: not detected).

	Date	Nicotine	Atenolol	Metamizole	Paraxanthine	Caffeine	Fluoxetine
Irrigation water (sprinkler)	03/11/09	143.2 ± 9.7	58.1 ± 4.9	nd	108.3 ± 9.1	104.6 ± 6.2	67.7 ± 8.6
Lysimeter	02/03/09	947.0 ± 64.4	nd	nd	nd	293.0 ± 17.3	nd
	12/03/09	1344.1 ± 91.4	nd	nd	52.0 ± 4.4	291.9 ± 17.2	nd
Water gallery	07/05/09	63.7 ± 4.3	1.7 ± 0.1	nd	49.8 ± 4.2	148.1 ± 8.7	nd
	14/07/09	95.8 ± 6.5	nd	nd	nd	21.5 ± 1.3	nd
	03/11/09	143.2 ± 9.7	11.2 ± 0.9	nd	14.5 ± 1.2	115.6 ± 6.8	nd
Well 3	29/04/09	39.0 ± 2.7	nd	nd	nd	33.7 ± 2.0	nd
	29/07/09	27.9 ± 1.9	nd	nd	nd	101.7 ± 6.0	nd
Well 4	29/04/09	64.6 ± 4.4	nd	nd	6.6 ± 0.6	53.6 ± 3.2	nd
	13/07/09	36.5 ± 2.5	nd	nd	nd	17.3 ± 1.0	nd
	03/11/09	54.1 ± 3.7	8.6 ± 0.7	nd	nd	24.9 ± 1.5	57.6 ± 7.3
Well 5	29/04/09	64.8 ± 4.4	nd	nd	nd	17.7 ± 1.0	nd
	13/07/09	49.7 ± 3.4	2.8 ± 0.2	nd	15.9 ± 1.3	41.4 ± 2.4	nd
	03/11/09	47.4 ± 3.2	nd	nd	nd	103.0 ± 6.1	nd
Well 6	29/04/09	55.6 ± 3.8	nd	nd	nd	30.9 ± 1.8	nd
	13/07/09	92.3 ± 6.3	nd	nd	nd	32.1 ± 1.9	nd
	03/11/09	58.5 ± 4.0	nd	nd	nd	22.0 ± 1.3	52.6 ± 6.7
Well 8	29/04/09	71.6 ± 4.9	5.0 ± 0.4	nd	33.0 ± 2.8	76.4 ± 4.5	nd
	13/07/09	39.6 ± 2.7	nd	nd	nd	19.6 ± 1.2	nd
	03/11/09	59.2 ± 4.0	nd	nd	15.1 ± 1.3	73.3 ± 4.3	nd

In the sampled wells, all the studied analytes were detected except for permethrin and metamizole. Figure 2 shows the graphical representation of the results for wells and gallery, where caffeine and nicotine were the most ubiquitous compounds, which confirmed their high and varied use. Moreover, these two compounds presented high concentrations throughout the year. The same occurred in the sample from the gallery. Finally, atenolol, paraxanthine, and fluoxetine were not detected throughout samplings.

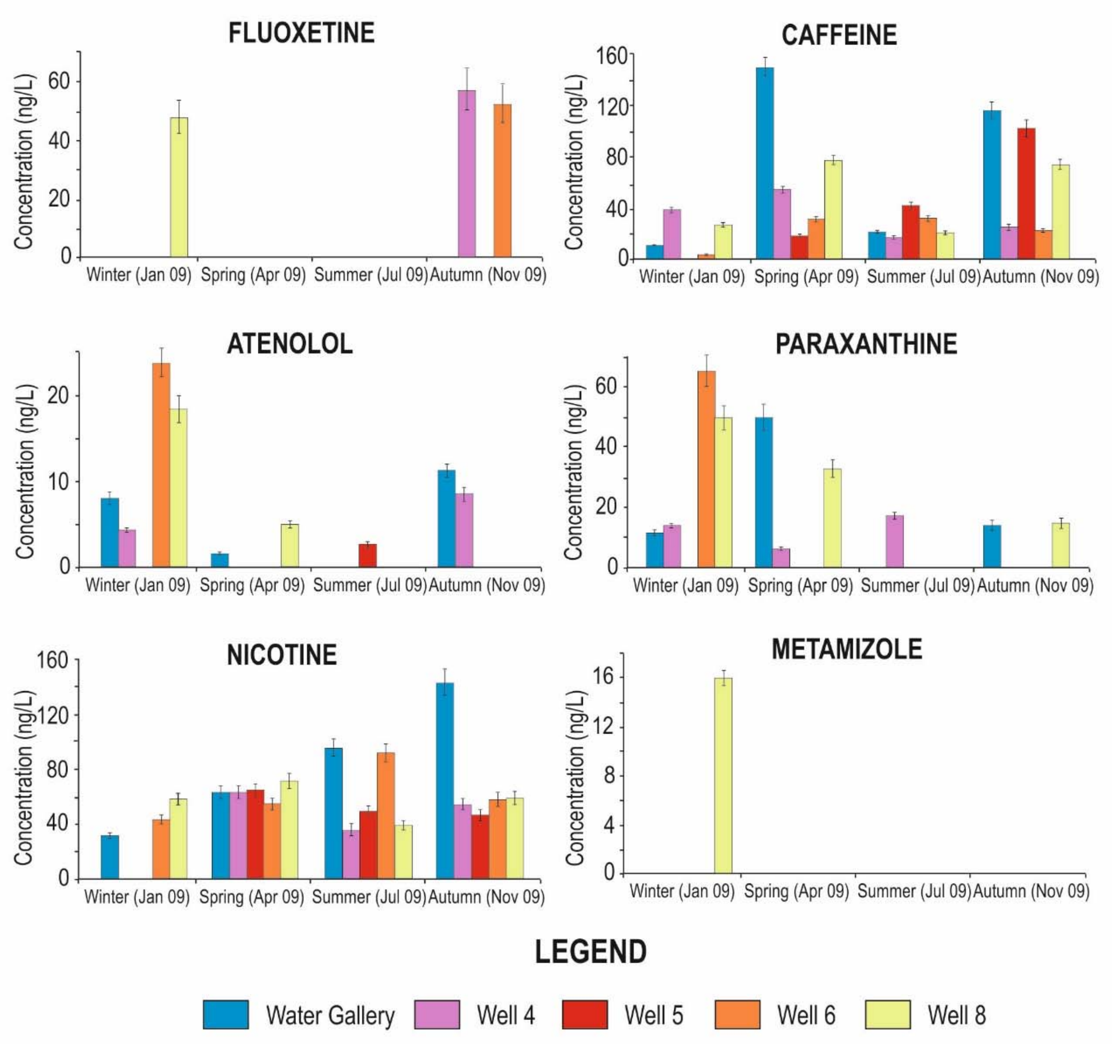

Figure 2. Seasonal occurrence and relative standard deviation (RSD) of target analytes in the groundwater samples from the wells control network. Well 3 is not represented because it was not sampled in all the campaigns. The locations of wells are included in Figure 1.

4. Discussion

Higher concentrations of compounds were found in the irrigation water sampled in the sprinkler than in the irrigation water sampled in the pond. The natural degradation of compounds is probably due to UV impacting on the pond surface (the sampling point), which could explain this result. Soil water was represented by the lysimeter samples, but it must be highlighted that the lysimeter only recovered water when soil field capacity was exceeded. Excess irrigation water was estimated at about 83% in Estevez et al. [27]. This excessive amount of reclaimed water used for golf course irrigation explains the similar concentrations measured in both irrigation water and the lysimeter during the initial sampling campaign.

After the water manager decided to apply lower irrigation water doses, the soil lixiviate sampled during all the following campaigns showed higher values than irrigation water, except for atenolol and fluoxetine. The accumulated adsorption of mobile compounds in soil when no water moved out of the root profile, followed by desorption processes coinciding with rainfall events, can explain these results. Although atenolol has a low adsorption capacity in clay minerals, a cation exchange-based adsorption mechanism has been described [28]. Its adsorption coefficients are positively related to oxidable organic carbon content, cation exchange capacity, basic cation saturation, salinity, clay content, or silt content [29], parameters with high values in the studied soils. Despite fluoxetine being shown to resist microbial degradation in soil, it presents a high log octanol/water partition coefficient (K_{OW}) of 4.05 [30]. Therefore, a finding of undetected fluoxetine concentrations in soil lixiviate is a consistent result. A previous study [4] demonstrated that pharmaceutical compound adsorption in volcanic areas not only responds to the soil properties commonly cited in adsorption studies, but also depends on andic properties, sorbent concentration, and dissolved organic carbon, the higher values of which are related to the lower distribution coefficient (Kd) and maximum adsorption capacity (Smax). Therefore, further studies are recommended to understand mobility processes of pharmaceutical compounds in volcanic soils. In the wells of the Las Goteras ravine, the contents of the analyzed compounds increased in the groundwater flow direction. This finding cannot be attributed only to golf course irrigation, but also to groundwater enrichment in emerging contaminants from different polluting sources, such as irrigation returns flows, septic tanks, or sewage system leaks [3], as pointed out in [9]. Thus, well 9 and well 10 had the highest concentrations, which coincides with the hydrogeochemical groundwater evolution made in the area, as reported in [5]. As indicated before, groundwater salinity increased towards the coast in the same way as emerging contaminants did. Well 6 is the deepest well in the network, and receives volcanic CO_2 contribution. This fact does not affect the existence of the compounds determined in its samples, which is attributed to the existence of preferential paths that are very common in volcanic terrains.

Nicotine and caffeine appeared in almost all the well samples, while atenolol and paraxanthine were found in at least half the samples. Atenolol has already been mentioned to present low adsorption capacity. In a study of emerging contaminants uptaken by two soils from Puerto Rico [31], paraxanthine was adsorbed only in the multicomponent test (probably only as a coadsorbate) and small amounts of caffeine were adsorbed. Thus, it is not unusual that soils fail in the retention processes of these compounds. During the initial campaign, metamizole and fluoxetine were detected only in four wells at concentrations up to 33.3 and 59.2 $ng \cdot L^{-1}$, respectively. These compounds were sporadically measured also in the control network. As fluoxetine presents a high log KOW, low concentrations in water and, therefore, low detection occurrence, can be expected. Only particular contamination events accompanied by preferential paths flow could explain these results. Figure 2 allows us to deduce the higher caffeine and nicotine values in the spring and autumn samples. The water gallery samples, especially, show a rise in the nicotine values from the first sampling to the last one (November 2009). Metamizole was absent in all these samples and had very low values during the first campaign. Degradation and adsorption phenomena through soil and the unsaturated zone could explain this result.

Nevertheless, if results are considered as a whole, they do not allow us to indicate any clear seasonal trend, but suggest the need to contemplate other factors, such as rainfall quantity, which is higher in autumn/winter. Atenolol and paraxanthine were more frequent in winter, which could suggest the unsaturated zone being quickly washed during the rainy season, and would be consistent with their aforementioned low adsorptions. In short, it would seem that the different behaviors of the analyzed compounds in soil, the vadose, and the unsaturated zone could play an important role in the results, and these aspects must be better studied.

Another aspect to consider is the comparison made of the results herein presented and the determinations made by the Analytical Chemistry at Laboratory the University of Jaén (UJ). These data, among many other determinations, are included in [9]. Nicotine, caffeine, and atenolol were analyzed in both laboratories with samples taken on the same day during the July and November 2009 campaigns (Figure 3). The analyses carried out at the University of Jaén also employed LC coupled to mass spectrometry, specifically with a time of flight (TOF) detector after using Oasis HLB SPE cartridges and methanol as an eluent. Regarding validation parameters in the UJ laboratory, seven replicates were performed to evaluate precision, obtaining good RSD (%) as well as good recovery rates. The obtained RSD values for atenolol, caffeine, and nicotine were 5.7, 9.1, and 15.6 %. The LODs and

LOQs fell within the 0.2–1.5 to 0.5–5 ng·L^{-1} range, respectively. pH was not adjusted as in the present study, so it could infer some differences in the retention of analytes in the cartridge. Moreover, when comparing the results obtained between laboratories, the trace levels at which the target analytes are measured must be considered.

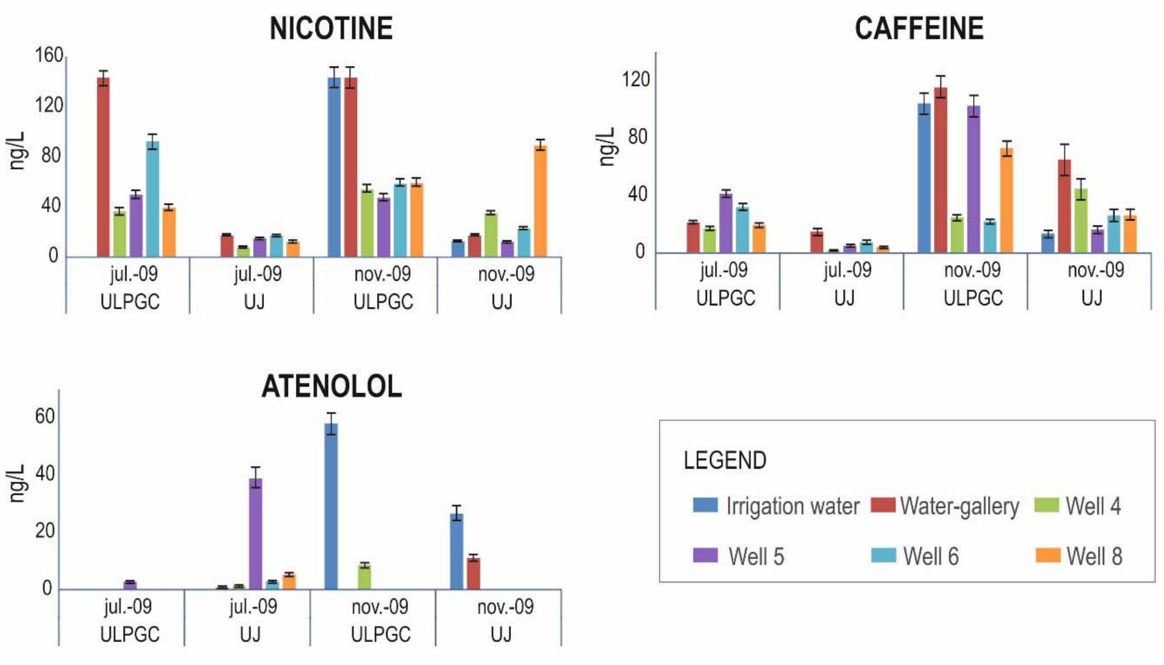

Figure 3. Comparison of the determinations and RSD of nicotine, caffeine, and atenolol obtained from the laboratories of University of Las Palmas de Gran Canaria (ULPGC) and the University of Jaén (UJ). Samples were taken on the same days for each campaign.

As observed in the comparison between the determinations by the two laboratories (Figure 3), most of the ULPGC laboratory values were higher than those from the UJ, especially for nicotine and caffeine. The results for atenolol were not as clear, and this pharmaceutical compound probably presented problems while treating samples in relation to either the retention or elution from the cartridge. In both cases, samples were taken in 1-litre amber glass bottles with Teflon caps, but differences were attributed to the time between sampling and the analysis, and to the sample conservation conditions during transport. In the ULPGC laboratory, samples were analyzed within 48 h of the sampling day and were immediately refrigerated. The samples for the UJ laboratory were sent by urgent mail services inside ex-profeso designed containers. Nevertheless, the transport from the island to the UJ could take 3 days at the best, and cold storage could not be guaranteed. Once samples arrived at the UJ laboratory, they were frozen and analyzed as soon as possible. Therefore, it is preferable to follow an in-situ solid-phase extraction procedure for isolated zones to isolate and preconcentrate the target analytes from samples, and then transport the obtained cartridges (with the concentrated samples) to the lab.

5. Conclusions

The optimized SPE–HPLC–ESI–MS/MS procedure allowed us to determine the target pharmaceutical compounds from different water samples in a simple, reliable, and rapid way.

Although reclaimed water is an important resource in dry regions, such as the Canary Islands, and even soil and the unsaturated zone can favor the natural removal of some pollutants, the presence of pharmaceutical residue must be controlled to evaluate the sustainability of reuse.

The presented study shows how previous hydrogeological studies must be carried out to better understand the behavior of pharmaceutical contaminants in aquifers. Almost all the analytes were detected while monitoring was carried out in the irrigation water and groundwater from the studied hydrological basin in the NE area on the Gran Canaria Island (Spain). A limited environmental risk was detected as low concentrations of pharmaceuticals were measured in the sampled wells, but they were always below 60 $ng \cdot L^{-1}$ (lower than those detected for caffeine and nicotine concentrations). Wide variations for the same well were measured between sampling campaigns, and also among different wells. In this area, it was not possible to establish the origin of the detected contamination in the aquifer, because it integrates different sources of water, in addition to the reclaimed water returns from the golf course irrigation, such as the septic tanks located along the ravine, water from breaks in the sewerage network, and irrigation returns of reclaimed water from neighboring small farms.

The comparison between the results from the two laboratories points to the importance of sample conservation during transport and the need to perform analyses immediately, but a set of representative samples through time should be analyzed to confirm this hypothesis. Another possibility is to follow an in-situ solid-phase extraction procedure to isolate and concentrate analytes from samples and to transport the obtained cartridges to the lab.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4441/13/3/262/s1, Table S1: Mass spectrometer parameters for the detection of target analytes, Table S2: Analytical parameters of the HPLC-ESI-MS/MS determination procedure.

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