

Article

Identification of Aquifer Recharge Sources as the Origin of Emerging Contaminants in Intensive Agricultural Areas. La Plana de Castellón, Spain

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Abstract: In urban, industrial, and agricultural areas, a vast array of contaminants may be found because they are introduced into the aquifers by different recharge sources. The emerging contaminants (ECs) correspond to unregulated contaminants, which may be candidates for future regulation depending on the results of research into their potential effects on health and on monitoring data regarding their occurrence. ECs frequently found in wastewater, such as acetaminophen, carbamazepine, primidone, and sulfamethoxazole, may be good indicators of the introduction of the reclaimed water to the aquifers. The resistance of the ECs to removal in wastewater treatment plants (WWTPs) causes them to be appropriate sewage markers. Plana de Castellón (Spain) is a coastal area that has been characterized by intensive citrus agriculture since the 1970s. Traditionally, in the southern sector of Plana de Castellón, 100% of irrigation water comes from groundwater. In recent years, local farmers have been using a mixture of groundwater and reclaimed water from wastewater treatment plants (WWTPs) to irrigate the citrus. The aims of the present study were: (i) to assess the occurrences, spatial distributions, and concentrations of selected ECs, including 32 antibiotics, 8 UV filters, and 2 nonsteroidal anti-inflammatory drugs, in groundwater in a common agricultural context; (ii) to identify the recharge (pollution) sources acting as the origin of the ECs, and (iii) to suggest ECs as indicators of reclaimed water arrival in detrital heterogeneous aquifers. The obtained data provided relevant information for the management of water resources and elucidated the fate and behavior of emerging contaminants in similar contexts.

Keywords: emerging contaminants; water resources management; groundwater pollution; pharmaceutical compounds

1. Introduction

The deterioration in groundwater quality has become a major issue for many aquifers. In urban, industrial, and agricultural areas, a vast array of contaminants may be found because they are introduced into aquifers through different recharge sources. Moreover, groundwater can be an alternative source

of water supply in areas with arid to semiarid climates. A proper assessment of groundwater quality is mandatory. Emerging contaminants (ECs) are compounds with different origins and chemical natures whose presence in the environment, or the related possible consequences of which, have largely gone unnoticed [1]. These compounds may have been recently identified as new pollutants or are not currently recognized as such; the presence of ECs in the environment has been detected due to the development of new and increasingly sensitive analytical methods [2,3]. The ECs include a wide variety of compounds (and their metabolites), such as pharmaceuticals, industrial products, abused drugs, and personal care products [4–10]. Their potential ecological and health effects have caused growing concern [11–13]. The ECs correspond in most cases to unregulated contaminants, which may be candidates for future regulation, depending on the results of research into their potential effects on health and monitoring data regarding their occurrence. The studies related to ECs can generally be categorized into three main groups: (1) assessments of occurrence in surface waters, such as rivers, wastewater, and treated water (e.g., water from a wastewater treatment plant, WWTP) [3,11,12,14–20]; (2) assessments of the fate and occurrence in groundwater (mainly in urban areas) [21–29], and (3) studies in agricultural areas where water demand is higher than the available natural resources and where wastewater, WWTP effluents, and reclaimed waters constitute an important source for irrigation. Irrigation with treated wastewater (WW) constitutes an important potential pollution source that can affect the crops, soil, groundwater, and associated ecosystems. As an example, it has been known since the 1970s that the use of pesticides (e.g., atrazine) in Mediterranean crop areas had been increasing until recent years, when both the land users and the public administration became aware of the potentially harmful effects on ecosystems and human health [28,30–35], among others.

Furthermore, according to directive [36], groundwater is the largest body of freshwater in the European Union, but it is also the most sensitive [23]. Thus, a proper assessment of groundwater quality requires the identification of potential pollutants derived from sources, such as irrigation water, to preserve groundwater quality and to allow its consumption or use, thus preventing potential health problems [37].

The southern part of La Plana de Castellón (Spain) (Figure 1) is a coastal area that has been characterized by intensive citrus agriculture since the 1970s. Traditionally, in the southern sector of Plana de Castellón, 100% of irrigation water comes from groundwater. During more recent decades, farmers have been using a mixture of groundwater and reclaimed water from a wastewater treatment plant (WWTP) to irrigate citrus crops. This method is used due to the scarcity and low quality of hydric resources (e.g., groundwater) in some drought periods, during which time the salinity is notably increased by seawater intrusion. As a result, a wide range of organic pollutants can be found in these aquifers.

The aims of the present study were: (i) to assess the occurrence, spatial distribution, and concentration of selected ECs found in treated wastewater in a common agricultural context; (ii) to identify the recharge (pollution) sources as the origins of the ECs, and (iii) to suggest ECs as indicators of reclaimed water arrival in detrital heterogeneous aquifers.

The study area was selected because it has been accurately characterized in previous hydrogeological studies and because preceding studies have reported the occurrence of different pollutants and ECs in waters from this area. The results of this study would help to enhance our understanding of the spatial occurrence of ECs in similar contexts (hydrogeology: aquifer, groundwater, etc.) and to also provide indications of the potential effects of the intensive use of reclaimed water (WWTP) for irrigation in agricultural areas.

2. Materials and Methods

2.1. Site Description

Along the Spanish Mediterranean coast, there are a number of coastal plains (aquifers) that accommodate a series of mostly detrital aquifers of great hydrogeological interest. Their flat morphology

extends from sea level (east) to their maximum elevations inland (west). The study site (the Rambleta area, Plana de Castellón aquifer) presents these typical characteristics (Figure 1). This area has a Mediterranean climate characterized by gentle winters, hot summers, and irregular rainfall. From 2007 to 2016, the mean annual rainfall was 506 mm/y and ranged from 696 to 286 mm/y [38]. This area, formerly devoted to agriculture (mostly citrus crops), now supports some small industrial settlements and villages. The high water demand brings about intense and continuous exploitation of both surface and groundwater resources. Intensive groundwater exploitation, until the late 1970s, caused seawater intrusion that affected a significant portion of the study area and resulted in a subsequent decrease in groundwater quality [39,40].

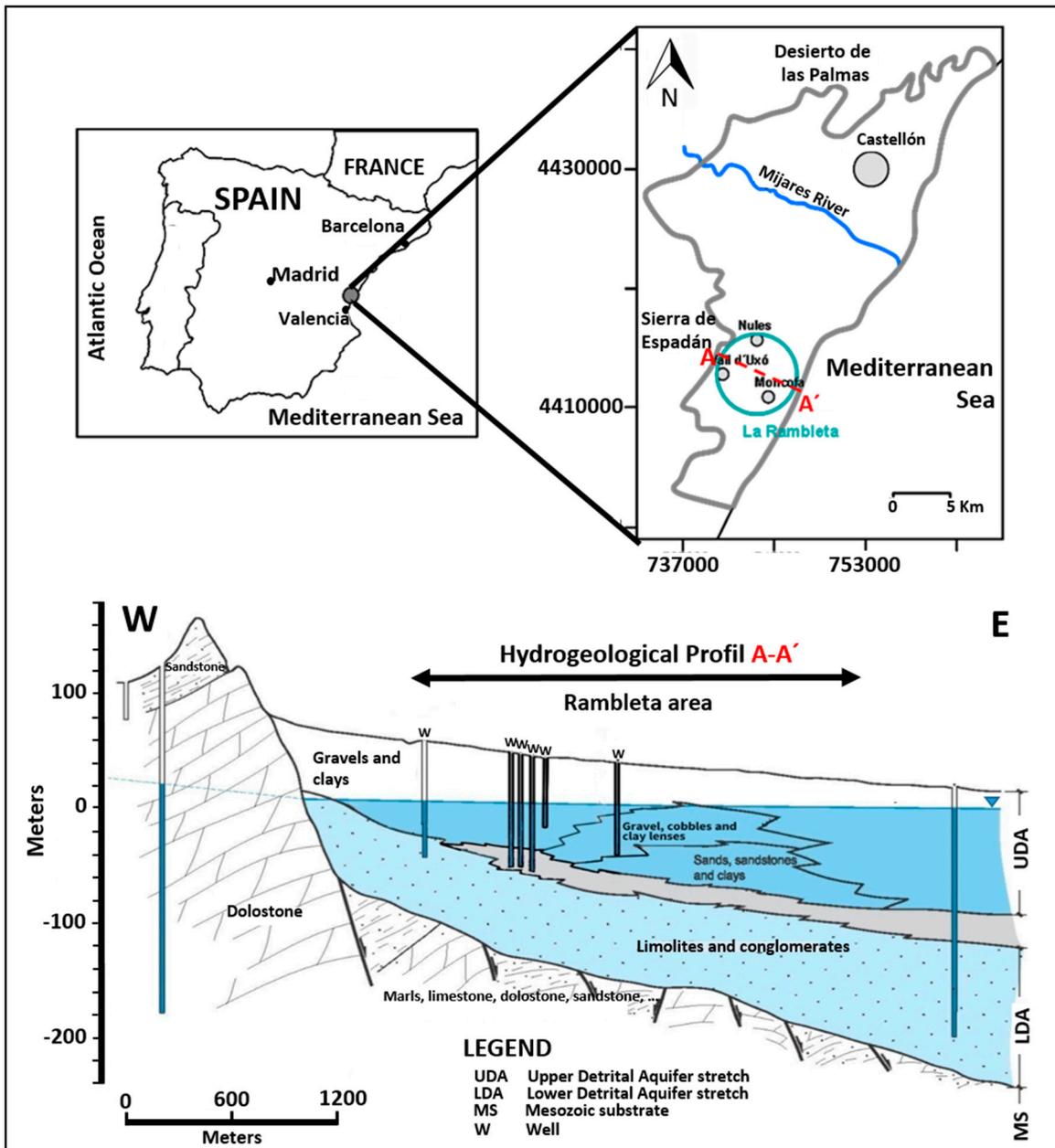


Figure 1. The situation of the study area (the Rambleta area, Plana de Castellón aquifer, Spain) and a hydrogeological cross-section through the study area [50].

The different studies conducted in the southern part of La Plana de Castellón aquifer provide details of the geology [41] and the hydrogeology [42,43]. Specific topics have also been addressed, such as studies on salinization, seawater intrusion, and groundwater contamination (e.g., by heavy metals, EC, and nitrate) [28,39,40,44–49].

Regarding the socio-economic context of this area, it is noted that the main activity is citrus agriculture, although sheep farms and small bullfighting farms are also located around the Rambleta area. It is interesting to highlight the industrial activity of the area, with an industrial site located east of the Rambleta area. Additionally, there is an extensive network of pipes that connects irrigation ponds with irrigation wells, which are used to transfer water between zones in times of water scarcity or poor groundwater quality.

2.2. Hydrogeological Setting

The La Plana de Castellón aquifer consists of layers and lenses of conglomerates, sands, and gravels—intercalated and contained within a silty-clay series—making up a single Plio-Quaternary aquifer unit (Figure 1). In general, the predominance of clayey material soil as opposed to soil with high organic matter content is a fact. It is a tectonic basin formed during the Tertiary as a result of the Neogene distension that generated a complex of horsts and grabens that continue beneath the sea. In the Rambleta area, two formations are recognized: upper and lower detrital aquifers—the upper detrital aquifer (UDA) and the lower detrital aquifer (LDA)—respectively [40]. The UDA (80–90 m depth) consists of conglomerates, sands, and gravels, with a significant proportion of fines. The LDA (50–100 m depth) contains a higher proportion of clays but also contains siltstones, sandstones, and conglomerates. The series overlies Mesozoic strata of variable permeability: Triassic limestones, marls, and dolomites (Muschelkalk facies), as well as orthoquartzite sandstones (Buntsandstein facies) and marls with gypsum (Keuper facies). The UDA hydrodynamic parameters show high variability, for which the transmissivity falls between 500 m²/d and 6000 m²/d (higher near the coast), and the permeability ranges from 40 to 110 m/d. The storage coefficients are between 5 and 15%, which is characteristic of an unconfined detrital aquifer. The typical pumping wells have a specific capacity range between 5 and 10 L/s/m. The UDA permeability is quite high and is exploited by most of the wells; the LDA is not exploited as extensively, as it is less permeable [39,51].

Prior to the exploitation scenario (1970–1980), groundwater flowed from the higher areas towards the sea following an NNW-SSE direction. The gradient was smooth, and the piezometric surface was similar to the topographic slope. Since the 1970s, the study area has supported significant agricultural activity. Before 1970, the amount of groundwater pumped in the Rambleta area was approximately 5 million m³/y. This pumping water reached a maximum in the mid-nineties with a total extraction of approximately 25 million m³/y; however, this value was progressively decreasing after this peak and has reached 14 million m³/y in recent years [40]. The causes of the decreasing need for groundwater extraction were as follows: (1) the irrigation system was modernized and optimized and (2) due to loss of groundwater quality, the reclaimed water from the Vall de Uxó WWTP, located 2 km SSW from the study area, supplied a few irrigation ponds and other facilities for agricultural irrigation purposes. As a result, approximately 2.5 million m³/year has been incorporated into the irrigation network.

Due to groundwater exploitation, the groundwater heads have changed markedly since 1970. Presently, a significant drawdown can be identified between the coast and the Rambleta area. The contour lines of the groundwater heads (Figure 2) show two minima, one in the west and the other in the center of the area. These two depressions modify the natural groundwater flow direction and have caused a notable increase in seawater intrusion due to a significant upconing process [40].

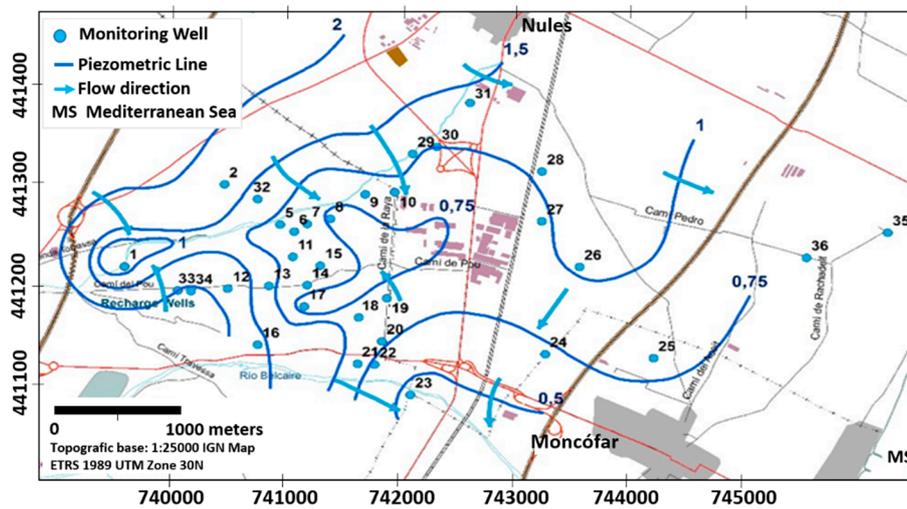


Figure 2. Piezometric map of the Rambleta area, October 2012 (modified from [40]).

As a consequence of the situation described, the local groundwater hydrochemistry shows three main impacts: (1) salinization by seawater intrusion (i.e., chloride concentrations greater than 700 mg Cl/L in the central part of the seawater upconing area); (2) high concentrations of compounds related to fertilizers and agro-chemicals, and (3) contamination with various urban wastewater compounds (e.g., nitrogen and detergents) due to the use of reclaimed WWTP water for irrigation, as shown in Figure 3.

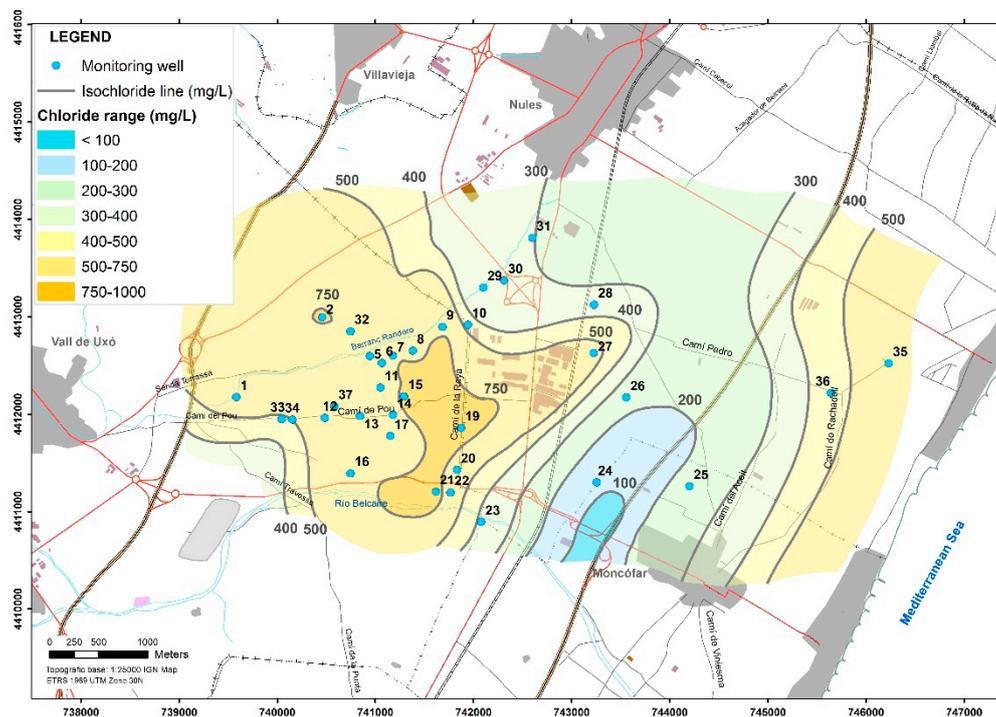


Figure 3. Cont.

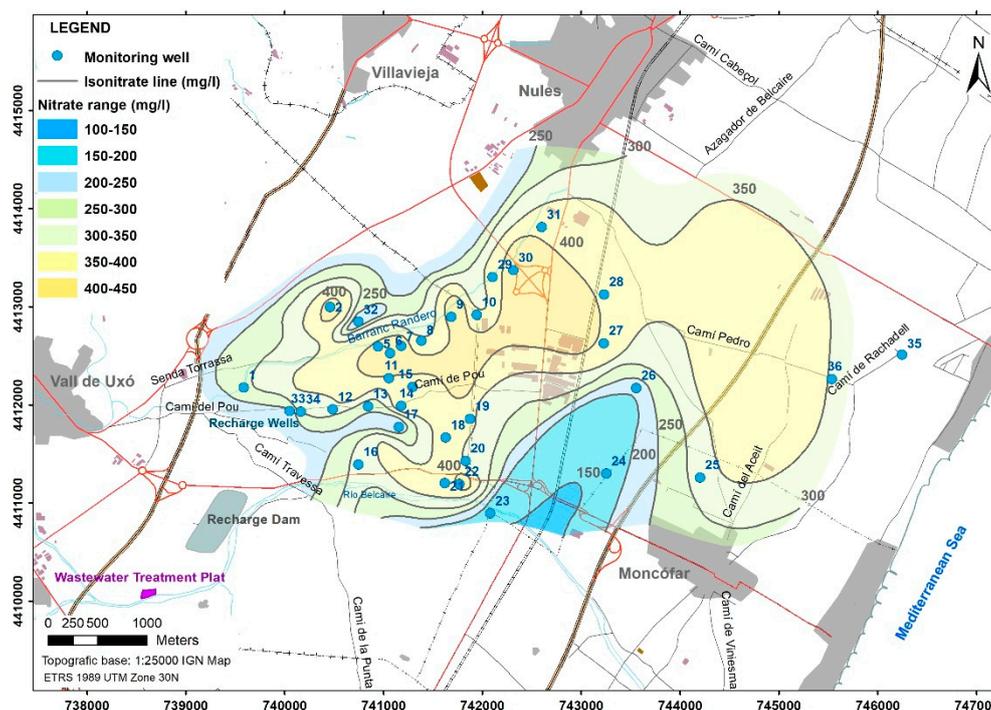


Figure 3. Maps of chlorides (up) and nitrates (down) concentrations in the Rambleta area, October 2012 (modified from [40]).

2.3. Monitoring Network and Sampling

To perform this study, 9 sampling points were selected. One sample corresponded to the effluent of the WWTP (EWW), another was collected from a freshwater dam (FW-D), and seven were groundwater samples (GW). Two surveys were carried out in this research; the first survey was in February 2015, and the second was in April 2015. Table 1 summarizes the main properties of the sampling points, and their geographical locations are shown in Figure 2.

Table 1. Identification of the sampling points.

Code	Type of Water	Total Depth (m)	Coordinate (X) ETRS 89	Coordinate (Y) ETRS 89	Observations
EWW	WWTP Effluent	-	738,588	4,410,027	2 samples per survey (1 in weekend, 1 during the week)
FW-D	FW-D Effluent	-	739,123	4,410,796	Fresh water dam
GW-1	Groundwater	51	741,869	4,411,851	Agricultural well. Abandoned
GW-2	Groundwater	100	739,579	4,412,167	Agricultural well
GW-3	Groundwater	42	741,058	4,412,523	Agricultural well
GW-4	Groundwater	100	740,485	4,411,955	Agricultural well
GW-5	Groundwater	NA	740,583	4,412,081	Piezometer. Abandoned
GW-6	Groundwater	100	740,054	4,412,034	Piezometer
GW-7	Groundwater	100	740,235	4,411,950	Piezometer

EWW: Effluent wastewater; WWTP: Wastewater Treatment Plant; FW-D: Freshwater Dam; GW: Groundwater; NA: Not Available.

FW-D samples were collected from the freshwater dam water. The GW samples were obtained at a depth of 5 m below the groundwater level by using a discrete interval sampler (Solinst 425) with a controlled opening mechanism. In all cases, the same technical sampling protocol was followed. Water samples were collected in 1 L opaque plastic bottles. The EWW was a 24 hours composite sample. The samples were directly stored in a portable refrigerator and were conserved at 4 °C until

the reception at the laboratory within a maximum of 8 h after sampling. The samples were then frozen at <-18 °C until analysis.

2.4. Characteristics of the Wastewater Treatment Plant (WWTP) and Freshwater Dam (FW-D)

2.4.1. Wastewater Treatment Plant (WWTP)

The Vall de Uxó WWTP is located 2.5 km to the south of the Rambleta area. It provides service to 31,819 inhabitants [52], with an approximate daily treatment volume of 4081 m³ [53]. The treatment system consists of two lines—a sludge line and a water line—which provide pretreatment, primary, and secondary treatment. A percentage of the EWW volume is directly spilled to a pipeline that ends in an irrigation pond, which is owned by the farm communities. The water in the irrigation pond is used during periods of hydric necessity, and the rest of the EWW volume flows into the Belcaire River (ravine). Table 2 shows the results obtained by analyzing the EWW samples.

Table 2. Analysis of EWW samples in April 2013, 2014, and 2015, and of FW-D in April 2013. Main physicochemical properties.

Physicochemical Properties	EWW			FW-D
	April 2013	April 2014	April 2015	April 2013
CE (μS/cm)	1145	1947	1023	311
Na ⁺ (mg/L)	130	180	111	9
K ⁺ (mg/L)	20	27	16	2
Ca ²⁺ (mg/L)	85	101	75	32
Mg ²⁺ (mg/L)	35	47	28	14
Cl ⁻ (mg/L)	118	180	107	14
SO ₄ ²⁻ (mg/L)	188	225	106	34
HCO ₃ ⁻ (mg/L)	279	504	314	115
CO ₃ ²⁻ (mg/L)	0	0	0	-
NO ₃ ²⁻ (mg/L)	130	0	64	5
NO ₂ ⁻ (mg/L)	<0.05	0	0	0.66
NH ₄ ⁺ (mg/L)	<0.05	0	0	<0.05
PO ₄ ³⁻ (mg/L)	<0.05	0	10.20	-
SiO ₂ ⁻ (mg/L)	11.1	12.7	10.6	-
MnO ₄ K oxidability (mg/L)	29.7	19.9	23.2	-
pH	7.05	7.66	7.27	8.00

(-) Not analyzed.

2.4.2. Fresh Water Dam (FW-D)

The freshwater dam (FW-D sample) is located 2 km to the east of the Rambleta area. This FW-D has a capacity of 2×10^6 m³, with a maximum water depth of 12 m and an area of 0.2 km². The FW-D receives runoff water from the Belcaire River during periods of intense rainfall. From 2013–2014, a pilot project for an artificial recharge was conducted [50]. The aim was to improve the quality of the groundwater affected by seawater intrusion. For this purpose, the FW-D was used as a freshwater reservoir. During an artificial recharge test, the freshwater was carried through a pipeline and injected directly into the brackish aquifer through two injection wells. The total volume injected over 6 months (between November 2013 and May 2014) was 300,000 m³, and the freshwater plume did not reach the entire study area, only reaching the sector located further east [50]. The physicochemical characteristics of the water in the FW-D are shown in Table 2.

2.5. Analytical Methods

2.5.1. Instrumentation

A Waters Acquity ultra-performance liquid chromatography (UPLC) system (Waters, Milford, MA, USA) was interfaced to a triple quadrupole mass spectrometer Xevo TQS (Waters, Milford, MA, USA) equipped with an orthogonal Z-spray electrospray ionization interface (ESI). Further details of the instrumentation, as well as the reagents and chemicals used, can be found in the Supplementary material (SI 1.1 and 1.2).

2.5.2. Selection of Analytes

In this study, 20 selected compounds were investigated: 15 pharmaceuticals (acetaminophen, bezafibrate, carbamazepine, diclofenac, gemfibrozil, irbesartan, metoprolol, pantoprazole, phenazone, primidone, sulfamethoxazole, trimethoprim, valsartan, venlafaxine, and iopromide); the main metabolite of cocaine (benzoylecgonine); 2 herbicides (simazine and terbuthylazine), and 2 transformation products (TP) of atrazine (atrazine-desethyl (DEA) and atrazine-desisopropyl (DIA)).

The selection of the compounds to be investigated was made according to the DEMEAU (demonstration of promising technologies to address emerging pollutants in water and wastewater) European project criteria [54]: (i) presence in wastewater and drinking water supplies, (ii) environmental relevance, (iii) different chemical and physical properties, and (iv) availability of appropriate analytical methods for their quantification.

Different isotopically labeled internal standards (ILIS) were used to compensate for the matrix effect. Concretely, acetaminophen-d₄, carbamazepine 10,11-epoxide-d₁₀, diclofenac-d₄, ibuprofen-d₃, irbesartan-d₆, venlafaxine-d₆, sulfamethoxazole-¹³C₆, trimethoprim-¹³C₃, valsartan-d₈, venlafaxine-d₆, benzoylecgonine-d₃, and terbuthylazine-d₅.

2.5.3. Sample Preparation

Each water sample (2 mL) was centrifuged at 12,000 rpm for 10 min and spiked with 100 µL of 1 µg/L ILIS mix solution to give a final concentration in the sample of 50 ng/L. Then, 100 µL of the supernatant was directly injected in the UHPLC–MS/MS system.

2.5.4. UHPLC-MS/MS Method

A quantitative method was applied for the measurement of the compounds based on LC-MS/MS with a triple quadrupole (QqQ). Twelve of these compounds had previously been validated [55] at three concentration levels (10, 100, and 1000 ng/L) in ten different effluent wastewater and surface water samples. For the remaining 8 compounds (terbuthylazine, atrazine-desethyl (DEA), atrazine-desisopropyl (DIA), iopromide, metoprolol, phenazone, primidone, and simazine), full scan mass spectra and MS/MS compound-dependent parameters (e.g., cone voltages and collision energies) were optimized by direct injection of individual standard solutions. The majority of the compounds (17 out of 20) were measured by the ESI operating in positive ionization mode and using the protonated molecule (M+H)⁺ as the precursor ion. Only the pharmaceuticals diclofenac and bezafibrate were measured with negative ionization using (M-H)⁻ as the precursor ion.

To guarantee unequivocal identification and quantification of the positive findings, the three most sensitive Selected Reaction Monitoring (SRM) transitions (in terms of signal-to-noise ratio) were selected for each compound. The most abundant transition was used for quantification (Q), and the other two were acquired for confirmation (q₁, q₂). For gemfibrozil, only two transitions could be monitored because of its poor fragmentation. Regarding ILIS, only the most intense SRM transition was acquired. The MS/MS parameters, as well as the SRM transitions and retention times, are listed in Table SI-1 (Supplementary material).

As is well known, matrix effects are one of the main drawbacks of LC-MS/MS. For aquatic samples, the high complexity of the different water matrices considerably affected the recovery values

of some compounds. For the majority of the studied compounds, matrix effects resulted in ionization suppression and were more important in the EWW samples than in the GW samples. The use of ILIS was the preferred option to remove or compensate for the matrix effects. Nine compounds (carbamazepine, diclofenac, sulfamethoxazole, trimethoprim, acetaminophen, benzoylecgonine, irbesartan, terbuthylazine, valsartan, and venlafaxine) could be corrected with their own ILIS, and satisfactory values were obtained after applying the correction. Carbamazepine, gemfibrozil, iopromide, metoprolol, phenazone, DEA, DIA, and simazine were corrected using an analog ILIS (Table SI-2, Supplementary material). The selection of an analog ILIS was mainly based on the retention time similarities between the analytes and ILIS, as it was expected that both were affected by similar constituents of the matrix and/or by the chemical structure [11]. Bezafibrate, primidone, and pantoprazole were not drastically affected by matrix effects in the water samples tested and were quantified by external calibration using absolute responses.

To ensure accurate quantification, quality controls (QCs) were included in every batch of samples. The QCs were prepared with 6 different effluent wastewater and groundwater samples, which were spiked at three concentration levels—10, 100, and 1000 ng/L—with all the analytes. As seen in Table SI-2 (Supplementary material), the QC recoveries were satisfactory (in the range of 70–120%) for the majority of compounds in both water matrices at the three concentrations assayed. Nevertheless, the QCs (at 100 and 1000 ng/L) for the atrazine metabolites (DIA and DEA), using acetaminophen- d_4 as the ILI (isotopically labeled internal standard), presented recovery values from 63 to 128% in groundwater. Although the use of an analog ILIS does not always assure an efficient matrix effect correction [55,56], the recovery ranges were still acceptable for these metabolites (between 60 and 140%, as proposed in some guidelines) [57]. For the 8 compounds that had not previously been validated by [55], the LOQs (limit of quantification) were estimated for a signal-to-noise ratio (S/N) of 10 from QC sample chromatograms at the lowest level tested using the quantification transition. The limits of quantification in the GW were, in general, below 3.8 ng/L, while those in the EWW samples were lower than 8.2 ng/L for all compounds, with the exception of iopromide and DIA (21 and 10 ng/L, respectively).

As an example, Figure 4 shows a positive finding for phenazone in the EWW. The result was considered to be positive when the retention time and at least one experimental ion-ratio were within the established tolerances (± 0.1 min and $\pm 30\%$, respectively) when compared with a reference standard [57]. As could be seen, the three transitions showed a peak at the same retention time (3.37 min). Moreover, both q/Q ratio deviations were within the tolerance limits $< 30\%$ [57].

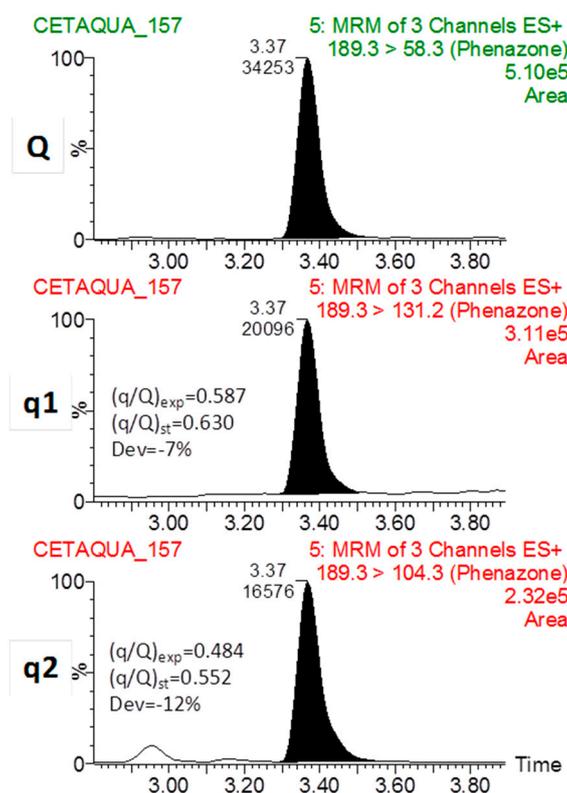


Figure 4. UHPLC-MS/MS chromatograms detected for a positive of phenazone in an EWW (effluent of the wastewater treatment plant) sample analyzed. (Q) corresponds to the transition used for quantification, and (q1) and (q2) to those used for confirmation. $(q/Q)_{exp}$: in the sample; $(q/Q)_{st}$ in the reference standard; Dev: deviation (%).

3. Results and Discussion

3.1. Assessment of the Occurrence, Spatial Distribution, and Concentration of Selected Typical ECs in Groundwater in a Common Agricultural Context

The EC concentrations (ng/L) found for each compound in the EWW, FW-D, and GW samples for both surveys are shown in Table 3, and an example is shown in Figure 4. In relation to the EWW, valsartan, used as an antihypertensive, was the compound with the highest concentration, with a value as high as 24 $\mu\text{g/L}$. Valsartan was followed by the contrast medium iopromide and the pharmaceuticals irbesartan and bezafibrate, all at concentrations above 1 $\mu\text{g/L}$. For the GW samples, bezafibrate, primidone, acetaminophen, sulfamethoxazole, and venlafaxine were found at the highest concentrations, although these were much lower than in the EWW, as expected, with maximum values of 10, 7.5, 6.5, 6.1, and 5.6 ng/L, respectively.

Although not all compounds were eliminated after the WWTP and were still detectable at different concentrations in the EWW samples, several compounds, such as diclofenac (analgesic), pantoprazole (proton-pump inhibitor agent), trimethoprim (antibiotic agent), and valsartan (hypertensive agent), were barely detected or not detected in the GW.

A wide majority of the compounds under study were found in the GW samples, although the decreases in concentrations relative to the EWW samples were remarkable. Data for diclofenac, irbesartan, and phenazone showed a similar trend, with very low concentrations found in only a few GW samples. There were several examples of decreasing concentration occurring from the EWW to the GW: one such example was irbesartan, with concentrations varying from 1547 ng/L (maximum concentration in the EWW) to below LOQ ng/L (0.2 ng/L) in most GW samples; diclofenac concentrations decreased from 802 ng/L (maximum concentration in the EWW) to below LOQ (3 ng/L)

in the GW, and phenazone concentrations decreased from 612 ng/L in the EWW to below LOQ (2.1 ng/L) ng/L.

The degradation rates of the compounds during the passage from the WWTP to the GW were greater than 90% (except for metoprolol, 86.5%). The less-frequently detected compounds were gemfibrozil, which was only found in the FW sample but not in the GW, and trimethoprim, which was quantified in only one GW sample; these compounds were followed by pantoprazole, valsartan, and phenazone, with 2, 5, and 5 positives, respectively. In contrast, bezafibrate, carbamazepine, irbesartan, and venlafaxine were found in 100% of the samples analyzed (Table 4).

The occurrence of bezafibrate in all samples analyzed, with concentrations ranging from 4.4 to 10 ng/L, agreed with previous studies by [58], who reported that bezafibrate, among other anionic species, exhibited low retention in clay soils, with its detection being feasible in GW. However, for carbamazepine, the results disagreed with [58], who showed that cationic/neutral species were retained in the clay soil and that they should not appear in the GW. In the present study, however, carbamazepine was found in the GW, although at very low concentrations. Several studies have revealed that this compound is considered to be highly stable in water/sediment [59], and, therefore, its presence in GW has been reported by a number of researchers [17,60–62]. Concerning venlafaxine, recent studies have indicated that it is not a compound that degrades easily and rapidly into its TP [63]. Therefore, this behavior might help to preserve the compound in the EWW during the process of irrigation and subsequent storage in the aquifer saturated zone. The antibiotic sulfamethoxazole exhibits a low soil sorption tendency because it is highly resistant to further biodegradation in the subsurface [64]. These characteristics allow the compound to be found in the GW samples. In the case of irbesartan, previous studies have confirmed the presence of this compound in GW [13], among others.

Recent studies of ECs around the world [15,65–70] have reported concentration values in the EWW in the same order as those found in this paper for the Vall de Uxó WWTP (Table SI-3, Supplementary material). The main differences between the EC values for the Vall de Uxó and those from previous works might be due to different consumption patterns of the citizens and the characteristics of the processes applied in the different WWTPs.

Table 3. The concentration of emerging contaminants (ECs) and pesticides analyzed in EWW, FW, and GW samples (2 sampling periods).

Compounds	Concentration (ng/L)											
	EWW				GW							
	LOQ	(A-B) 1*	(A-B) 2*	LOQ	FW-D	GW-1 (1*2*)	GW-2 (1*2*)	GW-3 (1*2*)	GW-4 (1*2*)	GW-5 (1*2*)	GW-6 (1*2*)	GW-7 (1*2*)
<i>Pharmaceuticals</i>												
Acetaminophen	1.5	106–44	42–36	1.1	<LOQ–10	4.8–<LOQ	6.5–(-)	<LOQ	<LOQ–(-)	2–<LOQ	3.3–1.7	63–<LOQ
Bezafibrate	2.1	1219–780	1095–1270	1.3	11–12	8.1–7.3	7–4.9	4.4–5	4.7–7.6	10–8.4	7.6–<LOQ	5–2.5
Carbamazepine	1.1	84–97	73–86	0.2	<LOQ	0.5–1.2	<LOQ	<LOQ	1.2–1.5	0.9–1.3	1.1–1.9	1.2–1.9
Diclofenac	7.2	538–408	769–802	3	-	3.6–(-)	3.1–(-)	4.6–(-)	-	-	-	-
Gemfibrozil	1.8	327–359	416–322	2.3	96–(-)	-	-	-	-	-	-	-
Irbesartan	1	1547–1123	1147–1246	0.2	<LOQ	<LOQ–0.3	<LOQ	<LOQ	<LOQ–0.3	<LOQ–0.3	<LOQ–0.3	<LOQ–0.3
Metoprolol	2.6	17–12	30–21	0.6	-	2.7–(-)	<LOQ–(-)	-	-	<LOQ–(-)	-	-
Pantoprazole	0.8	7.9–4.9	6.8–8.5	0.1	-	<LOQ	-	(-)-<LOQ	-	-	-	-
Phenazone	8.2	612–145	563–607	2.1	-	-	(-)-<LOQ	(-)-<LOQ	(-)-<LOQ	-	(-)-<LOQ	4.2–(-)
Primidone	4	151–57	37–28	1.1	<LOQ	(-)-<LOQ	<LOQ–2.9	<LOQ—	7.2–7.5	3.8–5.3	2.0–3.6	3.5–7.1
Sulfamethoxazole	0.8	140–115	153–158	0.5	<LOQ	4.1–<LOQ	<LOQ–4.4	(-)-<LOQ	6.1–4.7	3.4–2.8	<LOQ–4.8	<LOQ–3.6
Trimethoprim	2.3	103–81	145–102	1.8	-	<LOQ–(-)	-	-	-	-	-	-
Valsartan	4.2	23172–13509	23350–24283	3	9.2–18	3.1–<LOQ	<LOQ	-	-	-	-	3.3–(-)
Venlafaxine	1	962–619	831–801	0.2	1.1–<LOQ	5.6–1.3	1.2–1.4	<LOQ	<LOQ–1.2	<LOQ–1.5	<LOQ–1	5–1.2
<i>Contrast medium</i>												
Iopromide	21	1244–2362	2362–8616	7.6	-	-	<LOQ	<LOQ–(-)	<LOQ	<LOQ–(-)	<LOQ	<LOQ–(-)
<i>Drug of abuse</i>												
Benzoylcegonine	0.1	226–585	898–197	0.1	-	1.7–<LOQ	<LOQ–(-)	<LOQ	0.2–<LOQ	0.3–(-)	(-)-<LOQ	0.9–0.3
<i>Pesticides</i>												
Atrazine-desethyl (DEA)	3.6	11–12	-	1.8	-	5–9	11–18	15–(-)	19–19	11–11	9.2–9.0	14–18
Atrazine-desisopropyl (DIA)	3.4	16–19	-	1.7	-	5.2–6.1	<LOQ–1.9	3.6–(-)	4.5–4.1	4.0–4.6	<LOQ–2	<LOQ–2.9
Simazine	1.2	2.5–2.0	1.1–2.1	0.6	-	5.3–6.6	(-)-1	<LOQ–1.7	<LOQ–18	<LOQ–0.7	6.9–0.6	0.6
Terbutylazine	1	15–8.5	23–70	0.5	-	5.4–4.7	<LOQ–2.4	1.6–4.0	1–<LOQ	6.5–8.7	4.2–3.7	0.5–1

LOQ: Limit of Quantification; EWW: Effluent wastewater; FW-D: Freshwater Dam; GW: Groundwater; (-): Not detected; 1*: February 2015 survey; 2*: April 2015 survey; A: During the week sample; B: Weekend sample

Table 4. Percentage of degradation during the trajectory from the WWTP to the GW.

Compounds	Media EWW (ng/L)	Media GW (ng/L)	Degradation	Positive	Positive (%)	Quantified	Quantified (%)	Media EWW <150 (ng/L)	Positive (%) GW >85%	Degradation Compound <99%
<i>Pharmaceuticals</i>										
Acetaminophen	57	3.7	93.6	13	93	6	43	x	x	x
Bezafibrate	1091	5.5	99.9	14	100	13	114		x	x
Carbamazepine	85	1.3	98.5	14	100	10	71	x	x	x
Diclofenac	629	-	100	3	21	3	21			
Gemfibrozil	356	-	100	0	0	0	0			x
Irbesartan	1265	0.3	100	14	100	5	29		x	
Metoprolol	20	2.7	86.5	3	21	1	7	x		x
Pantoprazole	7	-	100	2	14	0	0	x		
Phenazone	481	4.2	99.1	5	36	1	7			x
Primidone	68	4.8	93	12	86	8	57	x	x	x
Sulfamethoxazole	132	4.2	96.8	13	93	8	57	x	x	x
Trimethoprim	107	-	100	1	7	0	0	x		
Valsartan	21078	-	100	5	36	2	14			
Venlafaxine	803	2.2	99.7	14	100	9	64		x	
<i>Contrast media</i>										
Iopromide	4739	-	100	10	71	0	0			
<i>Drugs of abuse</i>										
Benzoylcegonine	476	0.7	99.8	11	79	5	35.7			

3.2. Identification of the Recharge (Pollution) Sources as an Origin of the ECs

Potential sources of contamination located around the study area were diffuse (agriculture and livestock farming) or were spatially limited (closed and illegal small landfills and discharges into the Belcaire River) (Figure 5 and Table SI-4, Supplementary material).

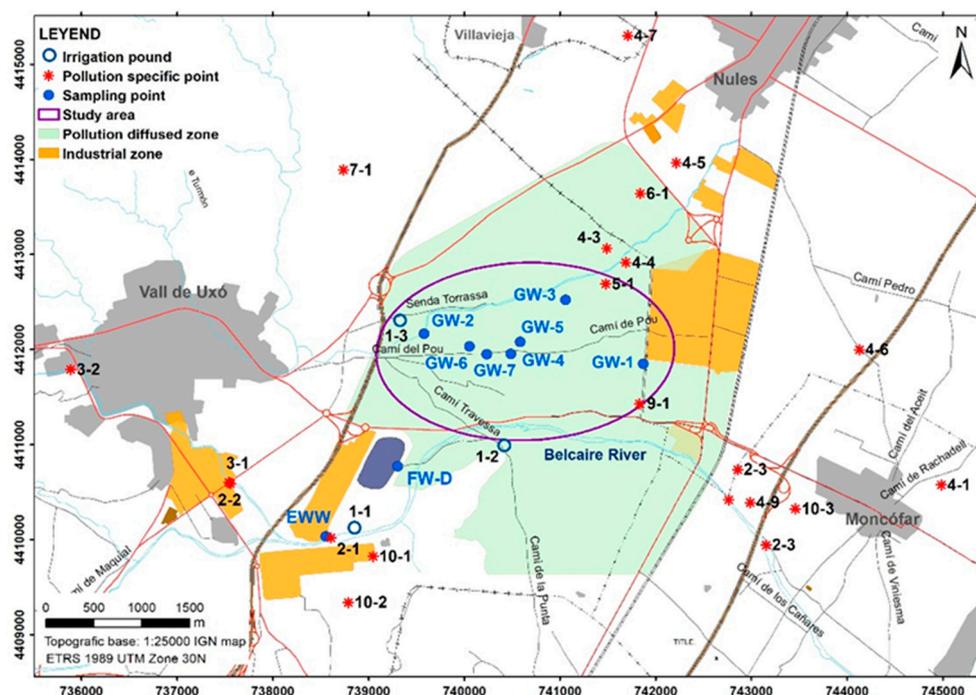


Figure 5. A real view of the Rambleta area and surroundings. Location of sampling points, pollution specific points, and pollution diffused areas.

Agricultural sources: Pesticides found in the water samples were herbicides from the triazine family. Specifically, simazine, terbuthylazine, and the transformation products—atrazine-desethyl (DEA) and atrazine-desisopropyl (DIA)—were detected; pesticide contamination was due to the agricultural practices in the area, which have been utilized intensively for more than 50 years (citrus fruit crops). The presence of pesticides in the surface waters and groundwater of this area has already been reported [28,71].

Concentrations of DEA (Figure 6) and DIA, simazine (Figure SI-2, Supplementary material), and terbuthylazine (Figure SI-3, Supplementary material), which were all detected in the GW, are summarized in Table 3. The concentrations found did not exceed 0.1 $\mu\text{g/L}$, the maximum allowed for pesticides in water for human consumption [37]. These herbicides are widespread and have been intensively used to control weeds in the Plana de Castellón area for decades. Although the use of simazine and atrazine on citrus was banned at the beginning of the 21st century, and terbuthylazine was banned some years ago (2010), they are still detected in the water. According to [72], the relatively high solubility of atrazine in water and its low absorption by the soil, as well as its persistence [73,74], can explain the detection of atrazine in water bodies even some years after its use. In Germany [75] and Finland [76], 10 years after the atrazine prohibition, this compound was detected in GW, sometimes without a trend of considerable decrease. Herbicide concentrations in groundwater vary from site to site, depending on the chemical behavior in various soil types, the particle sizes, organic matter contents, weather conditions (temperature and rain), and field management practices [76–78].

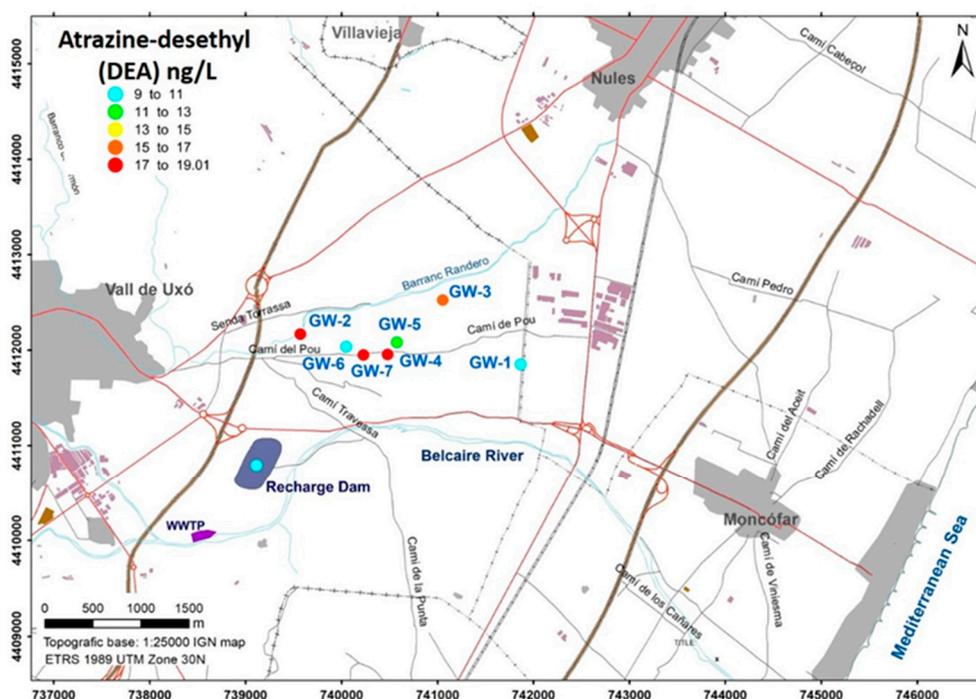


Figure 6. The location map of GW samples and the detected maximum concentrations of DEA (desethyl atrazine) (ng/L).

Reclaimed water and irrigation ponds (IP) sources: Irrigation in the study area is carried out with GW. Irrigation water is obtained directly from the well or is stored in irrigation ponds (IPs). In the case of IPs, water is distributed through a network of ditches and pipelines, and even among irrigation wells, there are underground pipes that communicate for water transfer. In periods of scarcity water (summer), water from IP is mixed with wastewater to meet irrigation needs, or it is directly watered with the reclaimed water. On the other hand, in times of extreme rainfall, the IPs drain the stored water through channels to the Belcaire River to avoid disasters or overflows. Considering that conventional treatment systems applied in WWTPs do not completely remove pharmaceuticals [15,79], it can be expected that some pharmaceuticals reach the groundwater, affecting the quality of the water. In this study, the main compounds found in the GW were bezafibrate, carbamazepine, venlafaxine, and sulfamethoxazole; see the distribution maps in Figure 7, case of carbamazepine, and remaining compounds maps are in the supplementary material (Figures SI-4, SI-5, and SI-6).

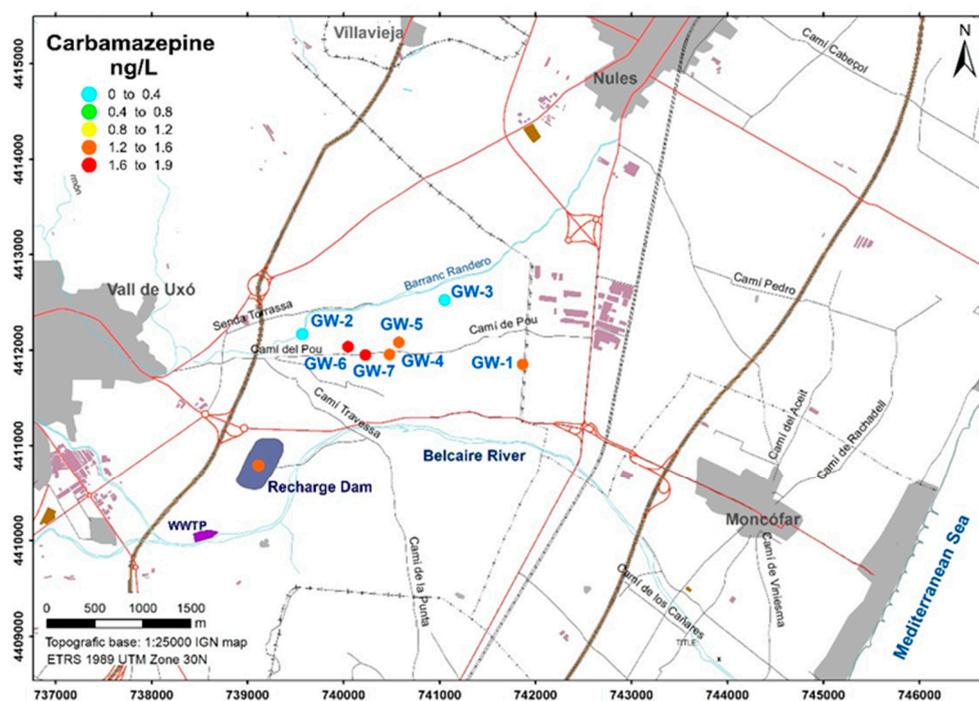


Figure 7. The location map of GW samples and the detected maximum concentrations of carbamazepine.

3.3. ECs Suggested to be Indicators of Reclaimed Water Arrival in Detrital Heterogeneous Aquifers through the Vadose Zone

According to data obtained in this work, seven compounds were proposed as indicators of the arrival of reclaimed water into the GW in aquifers with similar characteristics to the Rambleta area (i.e., a predominance of clayey material soil as opposed to soil with high organic matter content). These compounds were acetaminophen, bezafibrate, carbamazepine, irbesartan, primidone, sulfamethoxazole, and venlafaxine, which were detected in more than 85% of the GW samples, and of which only four (acetaminophen, carbamazepine, primidone, and sulfamethoxazole) showed low concentrations in the EWW (<150 ng/L). Additionally, the degradation of these four compounds was less than 99% (Table 4). Regarding these compounds, sulfamethoxazole exhibited a low soil sorption tendency because it is highly resistant to further biodegradation in the subsurface [64]. These characteristics surely allowed the compound to be detected in the GW samples. On the other hand, although acetaminophen was detected in this case, [80] showed that acetaminophen was degraded and not detected in GW, but they did not specify the soil types. In 2002, [81] pointed out that both primidone and carbamazepine were particularly useful for GW studies because both were detected. They were more recalcitrant than other compounds [26], but the aquifer characteristics were not specified. Carbamazepine may be a good indicator for soil with little organic matter and clayey characteristics, and it has been reported to also be appropriate for soils with high organic matter content [59]. Concerning venlafaxine, recent studies have reported that it is not easily and rapidly degraded into its TP [63]; this characteristic helps to preserve the compound in the EWW during the process of irrigation and subsequent storage in the aquifer saturated zone.

4. Conclusions

Considering that shortages of water resources in Mediterranean areas became a problem years ago, the use of reclaimed water for irrigation is a realistic alternative. This type of water resource will likely become one necessary source of medium-term subsistence if the estimated predictions of climate change and global population growth are fulfilled. Therefore, understanding the existence, behavior,

and persistence of these ECs in the GW are key to preserving GW quality against deterioration and are necessary to define environmental thresholds for large numbers of unregulated compounds.

The results of this study would help to enhance our understanding of the spatial EC occurrence in similar GW contexts, as well as to provide indications of the potential effects of intensive use of reclaimed water from WWTPs for irrigation in agricultural areas. The results obtained might provide important information for water resource management regarding the fate and behavior of persistent compounds (ECs and pesticides) in similar natural systems.

4.1. To Assess the Occurrence, Spatial Distribution, and Concentration of Selected Typical ECs in Groundwater in a Common Agricultural Context

The results show that ECs, including pesticides, have been detected in greater or lesser concentrations at all the sampled points, so the contamination affects the whole study area and not a particular sector. Presently, the conventional WWTPs (primary and secondary treatment systems) have low efficacy for removing most ECs; therefore, it is common to find these pollutants in the EWW, as has been corroborated in this study. On the other hand, it has been observed that in other locations of the planet, ECs and pesticides have been detected, which indicates that contamination is a global problem and not a local problem.

4.2. Identification of the Recharge (Pollution) Sources as an Origin of ECs

Although small sources of point pollution (illegal or closed landfills and old, contaminated discharges into the Belcaire River) are observed in the study area, irrigation with reclaimed water from the WWTP is the main source of pollution in the GW of the area. The pollutants (pharmaceuticals compounds) found in GW are those detected in the EWW, although they are detected at different concentrations. As for the ECs, their detection in the groundwater reveals their movement through the aquifer unsaturated zone, even when considering the area characteristics, such as drip irrigation, which occurs throughout the study area (optimizing the resource to the maximum), aquifers with predominantly clayey material soil as opposed to high organic matter soil and 15–40 m of vadose zone thickness. In the case of the studied herbicides (simazine, DIA, DEA, and terbutylazine), the persistence of these contaminants has been years, or even decades, after their use has been forbidden by the law.

4.3. Suggested Coes as Indicators of Reclaimed Water Arrival in Detrital Heterogeneous Aquifer

One of the indispensable tasks included in the management of this water resource is the control of contaminants. To conduct monitoring, detected ECs, such as acetaminophen, carbamazepine, primidone, and sulfamethoxazole, might be good indicators of the arrival of reclaimed water into the groundwater in aquifers with characteristics similar to the Rambleta area (unconfined aquifer, predominance of clayey material soil as opposed to soil with high organic matter content and 15–40 m of vadose zone thickness). In general, these compounds have been suggested as sewage (reclaimed water) markers due to their resistance to degradation in municipal WWTPs. These compounds are present at low concentrations in the EWW (<150 ng/L), but they also have been detected in the majority of analyzed groundwater samples, suggesting their tendency to reach groundwater. Among the named compounds, carbamazepine stands out because, in addition to being a good indicator for clayey soils with little organic matter, it has also been demonstrated to be appropriate for soils with high organic matter content [59]. On the other hand, it has been demonstrated that—independent of EWW—gemfibrozil, pantoprazole, trimethoprim, and valsartan should not be used as indicators of reclaimed water arrival to groundwater with the aforementioned characteristics because they have seldom been detected in GW samples even though their EWW concentrations are relatively high. Even valsartan, with a maximum EWW concentration of more than 23,000 ng/L, has only been detected in one GW sample with a concentration of 9.5 ng/L. This low rate of detection is due to the fact that this

compound can transform into its TP [63] and, to a small extent, to be retained in the vadose zone, which in this case has an average depth of 20 m.

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