Screening and Distribution of Contaminants of Emerging Concern and Regulated Organic Pollutants in the Heavily Modified Guadalhorce River Basin, Southern Spain

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Abstract: Emerging pollutants have aroused an increasing concern due to their ubiquitous presence in the environment and harmful potential. Both emerging (e.g., pharmaceuticals and personal care products) and regulated organic pollutants pose a serious threat to water quality and their presence and spatial distribution are complicated to address as they can derive from several factors: distribution of point and diffuse sources, environmental conditions, hydrogeological features of the region and inherent properties of the considered contaminants. In this study, a ground and surface water monitoring campaign was conducted in the three main detritic groundwater bodies of an extensive and heavily modified river basin in order to draft an initial description of the occurrence and distribution of a wide range of organic contaminants. In total, 63 out of 185 target pollutants were detected. An attempt to understand the importance of different factors governing the distribution of some of the most frequently found pollutants was made. Antibiotics spatial distribution is potentially influenced by the hydrogeological functioning of the basin modified by hydraulic infrastructures (reflected by hydrochemistry and environmental tracers δ²H and δ¹⁸O), not directly related to the distribution of potential sources. The presence of other organic pollutants does not reflect an evident correlation with flow pathways. Differences in contaminant occurrence are potentially attributed to the way pollutants are released into the environment as well as physico-chemical properties.

Keywords: emerging contaminants; organic contaminants; groundwater; environmental tracers; large scale

1. Introduction

Society today uses a broad array of synthetic organic compounds on a daily basis for purposes like household activities, industrial manufacturing, agricultural applications and human and animal healthcare. These chemical products as well as other organic compounds derived from anthropogenic activities have reached the terrestrial and aquatic environment, sparking a growing interest and concern about their environmental fate and toxicity [1]. Among these, pharmaceutically active compounds (PhACs) and personal care products (PCPs) are regarded as contaminants of emerging concern, many of them with unknown geochemical behavior, which may trigger undesirable effects.
on water resource availability in the long term. Moreover, their presence in the environment is largely unregulated by legislation. Currently, threshold values are established only for nitrates and pesticides for groundwater [2]. Nonetheless, some PhACs and PCPs have already been placed on a “Watch List” [3], so their presence in the aquatic environment could eventually be contemplated by EU legislation.

PCPs are a very important group of pollutants in terms of production volume. It includes fragrances, UV filters, insect repellents, antibacterials, surfactants and some new flame retardants, among others. Emerging pollutants do not need to be highly persistent to negatively affect ecosystems and human health [4–6] as their degradation is offset by a continuous input into the environment [7,8].

Emerging and regulated (e.g., pesticides and polycyclic aromatic hydrocarbons) organic contaminants enter groundwater from several sources, such as treated [9] or untreated domestic and industrial effluents, leachate from landfills, leakages in septic tanks and sewerage, agricultural practices (i.e., use of pesticides and irrigation with reclaimed wastewater [10]), livestock activities (i.e., waste lagoons and manure application to soil; [11]) and also indirectly through groundwater–surface water exchange processes [1]. In addition, special conditions such as the combination of extreme rainfall events and raw wastewater can cause a sewer overflow, resulting in significant loads of organic contaminants in some areas [12].

Once released into the environment, natural attenuation of organic pollutants depends on several processes such as dilution, hydrolysis, biodegradation and sorption, among others. Sorption processes in the subsurface depends on both their physicochemical properties and environmental factors [13]. The fate of non-ionizable compounds is determined by hydrophobic sorption, whereas the charge state of ionizable molecules can influence several key characteristics (e.g., volatility, hydrophilicity, reactivity, sorption affinity; [14]), which makes pH an important environmental condition. Other environmental factors playing an important role in organic pollutant attenuation are temperature and redox potential [15], which can also promote or limit biodegradation [11].

Consequently, a very uneven distribution of regulated and non-regulated organic pollutants in groundwater is expected at a large scale given the wide variety of factors involved: distribution of potential sources in the area, environmental factors, hydrogeological features of the region and physico-chemical characteristics of the considered compounds [16].

In this research, the presence of contaminants of emerging concern and regulated organic pollutants in groundwater in an extensive and highly modified river basin is assessed with the aim to provide an initial description of the area regarding water pollution by organic chemicals. To this end, a surface and groundwater monitoring campaign was carried out in detritic aquifers to investigate the spatial distribution and occurrence of 185 microcontaminants of different groups of classes: polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and pesticides; and emerging pollutants: PhACs, PCPs and organophosphorus flame retardants (OPFRs). Further research will be optimized based on the obtained results.

2. Study Area

The Guadalhorce River basin is located in southern Spain. It extends over an area of approximately 3200 km$^2$ and the length of the river is 166 km. As shown in Figure 1, the river is born in the northeast of the basin and flows into the Mediterranean Sea to the southwest of the city of Malaga. The climate characteristics of the area are mild temperatures, whose annual mean value varies from 13 °C to 18 °C, and a defined precipitation regime throughout the year: October to February are the wettest seasons when extreme events occur frequently, with summer (June to September) being the driest season. Rainfall values range from 400 to 500 mm/year in the southern part of the basin and from 900 to 1000 mm/year in the northern part [17].
Figure 1. The Guadalhorce River basin and the three target areas (A, B and C) with the sampling points.

The Guadalhorce river basin can be divided into two sectors due to the presence of a mountain range located in the center: the northern sub-basin whose flatlands are located at a higher altitude (between 300 and 600 m a.s.l.), and the southern sub-basin (between 0 and 200 m a.s.l. given the altitude of its flatlands) [17]. This division is also based on the hydrological functioning of the two sub-basins, which is influenced by the presence of three dams that collect water from the entire upper basin (Figure 1).

Three aquifer types have been identified in the basin: carbonate, porous and evaporitic [17]. Carbonate aquifers, whose springs feed the main surface watercourses, are formed by Mesozoic limestones, dolostones and marbles of the external and internal zones of the Betic Cordillera. The Malaguide Complex, a tectonic unit included in the internal zone, is on the right bank of the Guadalhorce River, near the city of Malaga, and contains greywackes and phyllites (shales) with disseminated pyrite and organic matter [18].

The Triassic clay, sandstone and evaporative material (gypsum and halite) outcrops [17] form the only evaporitic aquifer, which is in the northern sub-basin. These materials also constitute the basement of the porous and carbonate aquifers of the basin.

The target areas of this work are three porous aquifers located in the flatlands of the basin: the Lower Guadalhorce (sector A; Figure 1), situated in the lower part of the basin, and Vega de Antequera-Archidona (sector B; Figure 1) and the Teba-Almargen-Campillos area (sector C; Figure 1) situated in the upper sub-basin.

In sector A (Lower Guadalhorce), the Quaternary and unconfined aquifer is formed by alluvial sediments such as gravels, sands, silts and clays. The underlying rocks are Upper Miocene calcareous sandstones and conglomerates, and Pliocene conglomerates, marl and sand layers. Pliocene sediments can be 300 m thick and, at the bottom of the series, conglomerates form a discontinuous confined
aquifer underlying the marls. At a shallower level, interrupted sand layers act as a semiconfined aquifer (Figure 2 [19–21]).

The Vega de Antequera-Archidona aquifer (sector B) consists of Neogene and Quaternary deposits such as calcareous sandstones and alluvial sediments [22].

The Teba-Almargen-Campillos (sector C) system is formed by two detritic aquifers and one carbonate aquifer that are hydrologically connected. Calcarenites, conglomerates and marls (Miocene) and detrital materials of fluvial origin (Quaternary) constitute the detritic aquifers and Jurassic limestones form the carbonate one [23].

Figure 2. Geological scheme of sector A (a) and hydrogeological section (b) (modified from [19–21]). Legend: 1: Quaternary aquifer formed predominantly by gravels and sands; 2: Quaternary aquifer consisting of sands, silts and clays; 3: low-permeability Pliocene clays and marls; 4: semiconfined Pliocene aquifer formed by gravels and sands.

3. Materials and Methods

3.1. Water Sample Collection and Preparation

In the March 2016 sampling campaign, 31 groundwater and surface water samples (Figure 1) were collected. Groundwater samples (21) corresponded to the porous aquifers and were collected
directly from the wells (<30–40 m deep) after continuous pumping; sample G26 was the only one collected using a submersible sampler. All water samples were filtered through a 0.45 µm Millipore® (Merck KGaA, Darmstadt, Germany) filter. Samples for hydrochemical and isotopic analyses were stored in sterile high-density polyethylene bottles (120 mL) sealed with inverted cone caps; sterile amber glass bottles (1 L) with Teflon caps were used for samples to be analyzed for organic compounds. All bottles were rinsed before sampling, carried in a cool-box and then stored in a fridge below 4 °C until analysis was performed, generally within 24 h of sampling.

In situ physico-chemical parameters: pH, temperature, electrical conductivity (EC), redox potential (Eh) and dissolved oxygen (DO) were measured with a portable multi-parameter probe Hach-Lange HQ40d (Hach, Loveland, CO, USA) and a flow cell to avoid contact with the atmosphere (Table 1). Electrical conductivity was calibrated with a NaCl standard solution. The pH was calibrated with 4 and 7 pH buffer solutions.

| pH     | EC (µS/cm) | Temperature (°C) | Eh (mV) | O2 (mg/L) |
|--------|------------|------------------|---------|-----------|
| Sector A |            |                  |         |           |
| Min.   | 7.0        | 1877             | 16.2    | 105       | 3.4       |
| Max.   | 9.1        | 4100             | 19.0    | 203       | 7.6       |
| Median | 7.4        | 2280             | 18.3    | 190       | 5.0       |
| Mean   | 7.5        | 2640             | 18.0    | 181       | 5.5       |
| Std. dev. | 0.6    | 777              | 1.0     | 32        | 1.7       |
| Sector B |            |                  |         |           |
| Min.   | 7.0        | 305              | 14.2    | 187       | 7.0       |
| Max.   | 7.7        | 2300             | 18.0    | 277       | 8.9       |
| Median | 7.1        | 1626             | 15.0    | 241       | 8.8       |
| Mean   | 7.2        | 1518             | 15.5    | 235       | 8.2       |
| Std. dev. | 0.2    | 631              | 1.2     | 27        | 0.8       |
| Sector C |            |                  |         |           |
| Min.   | 7.1        | 495              | 11.6    | 160       | 3.2       |
| Max.   | 8.3        | 3730             | 18.5    | 235       | 9.8       |
| Median | 7.4        | 1454             | 15.2    | 198       | 5.9       |
| Mean   | 7.5        | 1775             | 15.2    | 201       | 6.0       |
| Std. dev. | 0.4    | 1192             | 2.4     | 28        | 2.7       |

3.2. Hydrochemical and Isotopic Analysis

Hydrochemical analysis (Table 2) consisted in the determination of major and minor components (Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO₃⁻, Cl⁻, SO₄²⁻ and NO₃⁻) and it was performed using HPLC with a Metrohm 881 Compact IC Pro. δ²H and δ¹⁸O were determined with laser spectroscopy (CRDS) in a Picarro Water Isotope Analyzer L2120i. Notation for δ²H and δ¹⁸O is expressed in ‰ in relation to the international standard Vienna Standard Mean Oceanic Water (V-SMOW). Hydrochemical and isotope determinations were performed at the laboratory of the Center of Hydrogeology of the University of Malaga.
Table 2. Descriptive statistics for hydrochemical parameters and stable isotopes $\delta^2$H and $\delta^{18}$O of sectors A, B and C.

|        | Ca$^{2+}$ (mg/L) | Mg$^{2+}$ (mg/L) | Na$^+$ (mg/L) | K$^+$ (mg/L) | HCO$_3^-$ (mg/L) | SO$_4^{2-}$ (mg/L) | Cl$^-$ (mg/L) | NO$_3^-$ (mg/L) | $\delta^2$H (%) | $\delta^{18}$O (%) |
|--------|------------------|------------------|--------------|-------------|-----------------|------------------|--------------|---------------|---------------|----------------|
| Sector A | Min. 7.4          | 0.8              | 5.6          | 0.4         | 96.2            | 66.7             | 123.1        | 2.9           | $-31.8$       | $-5.1$         |
|        | Max. 283.8        | 138.9            | 526.3        | 7.6         | 474.4           | 233.5            | 694.3        | 58.5          | $-28.2$       | $-4.0$         |
|        | Median 115.5      | 80.7             | 207.5        | 3.9         | 371.7           | 186.2            | 234.1        | 18.9          | $-30.2$       | $-4.8$         |
|        | Mean 112.2        | 81.8             | 243.3        | 3.7         | 353.7           | 169.3            | 273.7        | 25.0          | $-30.0$       | $-4.6$         |
|        | Std. dev. 95.3    | 44.9             | 189.3        | 2.5         | 112.8           | 55.3             | 164.6        | 20.4          | 1.4           | 0.4            |
| Sector B | Min. 54.3         | 6.3              | 1.8          | 0.3         | 191.1           | 8.5              | 3.6          | 3.8           | $-43.5$       | $-7.6$         |
|        | Max. 316.0        | 82.2             | 165.9        | 3.7         | 301.0           | 2007.1           | 197.5        | 155.9         | $-34.8$       | $-5.0$         |
|        | Median 244.2      | 50.3             | 58.6         | 2.3         | 270.1           | 291.2            | 81.2         | 75.6          | $-37.5$       | $-5.8$         |
|        | Mean 208.3        | 48.6             | 67.2         | 2.3         | 260.7           | 786.9            | 82.4         | 70.0          | $-37.8$       | $-5.9$         |
|        | Std. dev. 99.2    | 26.7             | 50.7         | 1.0         | 40.9            | 823.2            | 62.0         | 44.8          | 2.5           | 0.7            |
| Sector C | Min. 57.6         | 10.6             | 13.6         | 1.6         | 243.7           | 20.3             | 10.4         | 5.5           | $-41.4$       | $-6.5$         |
|        | Max. 381.9        | 136.7            | 306.0        | 4.8         | 340.8           | 664.2            | 300.1        | 433.8         | $-33.3$       | $-5.2$         |
|        | Median 135.7      | 45.4             | 120.1        | 2.6         | 284.5           | 143.5            | 88.1         | 44.8          | $-36.5$       | $-5.6$         |
|        | Mean 160.6        | 57.8             | 130.2        | 2.8         | 285.5           | 242.3            | 105.9        | 108.4         | $-36.8$       | $-5.8$         |
|        | Std. dev. 129.0   | 52.2             | 113.8        | 1.3         | 35.7            | 265.3            | 113.9        | 183.2         | 3.4           | 0.6            |

3.3. Analysis of Emerging and Regulated Compounds

Chemical analysis on water samples of 185 microcontaminants was performed; selected target compounds are listed in Table 3. Analysis of pharmaceutically active compounds (PhACs) was performed by solid-phase extraction (SPE) followed by ultra-performance liquid chromatography– triple quadrupole mass spectrometry (UPLC-QqQ-MS/MS) using a Bruker EVOQ Elite system (Bruker, Billerica, MA, USA) equipped with an electrospray ionization source [24].

For personal care products (PCPs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organophosphorus components used as flame retardants (OPFRs) and several types of pesticides (organochlorine and organophosphorus pesticides, triazines and pyrethroids), samples were processed using stir bar sorptive extraction (SBSE) [25]. Separation, identification and quantification of target contaminants were performed using gas chromatography (SCION 456-GC, Bruker) coupled to triple quadrupole mass spectrometry (SCION TQ from Bruker with CP 8400 Autosampler) [26]. Analyses were conducted in the laboratory of the Marine Research Institute of the University of Cadiz.

Further information on the limits of detection, extraction recoveries and performance of the analytical methods used here can be found in the aforementioned references [24–26].

4. Results and Discussion

4.1. Water Chemistry and Hydrochemical Water Types

For all analyzed samples, pH values ranged from 7.0 to slightly alkaline (maximum pH of 9.1 in sector A). Eh maximum values are lower than 300 mV, reflecting weak anoxic conditions which are also revealed by low mean values of dissolved oxygen in sectors A and C. A summary of descriptive statistics for physico-chemical and hydrochemical parameters recorded in groundwater is presented in Tables 1 and 2.

Sectors A, B and C revealed EC values of up to 4100, 2300 and 3730 $\mu$S/cm, respectively, showing a high mineralization in some sampling points. The EC mean value in sector A can be explained by anthropogenic pollution sources and seawater influence in areas close to the sea border. High concentrations of sulfate in sector B (Table 2) constitute an important contribution to groundwater
mineralization in this sector. The basement of the porous aquifers, partly constituted by evaporitic materials (Triassic), is responsible for high natural background levels of dissolved $\text{SO}_4^{2-}$, especially in the upper basin (sectors B and C). However, in the lower basin, the high concentrations of dissolved $\text{SO}_4^{2-}$ are essentially a consequence of the use of fertilizers, which represents over 80% of the total [27].

The Piper diagram (Figure 3) reveals the occurrence of four water types or hydrochemical facies of the monitored groundwater: $\text{HCO}_3^{-}\text{-Ca}^{2+}$, $\text{SO}_4^{2-}\text{-Ca}^{2+}$, $\text{Cl}^{-}\text{-Na}^{+}$ and mixed types. Most samples from sector B reveal $\text{SO}_4^{2-}\text{-Ca}^{2+}$ facies, reflecting the influence of the evaporitic materials of the basement. Sampling points G1 and G12 ($\text{HCO}_3^{-}\text{-Ca}^{2+}$) drain carbonate materials. The chemical composition of G26 ($\text{Cl-Na}^{+}$), situated near the mouth of the Guadalhorce River, suggests seawater influence. Mixed types are essentially represented by water samples from the lower sub-basin (sector A), which means there are several processes or water sources involved in the formation of this water composition.

![Piper diagram showing hydrochemical facies of monitored groundwater from sectors A, B and C.](image)

**Figure 3.** Piper diagram showing hydrochemical facies of monitored groundwater from sectors A, B and C.

### 4.2. Organic Active Compounds

In total, 63 out of 185 target pollutants were detected in the study area (Table 3), of which 21 were found at least in 25% of the groundwater samples (Figure 4). On average, 17 compounds were detected per groundwater sampling point. The maximum number of contaminants was observed in G26 (55 compounds) located in sector A, near the mouth of the Guadalhorce River. The high presence of compounds is potentially due to a waste water treatment plant (WWTP, near Malaga City) located upstream and possible discharges from an existing industrial site.
### Table 3. Analyzed compounds, CAS (Chemical Abstracts Service) number and use. Legend: PCPs: personal care products; OPFRs: organophosphorus flame retardants; PAHs: polycyclic aromatic hydrocarbons; PCBs: polychlorinated biphenyls. Detected compounds are indicated in bold type.

| Compounds | Pharmaceuticals | CAS | Use | PCPs | CAS | Use | Pesticides | CAS | Use |
|-----------|-----------------|-----|-----|------|-----|-----|-------------|-----|-----|
| α-ethynylestradiol | 17α-ethynylestradiol | 57-63-6 | Estrogen | OD-PABA | 21245-02-3 | UV filter | Aldrin | 309-00-2 | Organochlorine pesticide |
| β-estradiol | 17β-estradiol | 50-28-2 | Estrogen | 2-OHB | 117-99-7 | UV filter | Atrazine | 1912-24-9 | Triazine |
| Acetaminophen | Acetaminophen | 103-90-2 | Analgesic/anti-inflammatory | 3-OHPB | 36302-57-0 | UV filter | Atrazine | 1610-17-9 | Triazine |
| Albuterol | Albuterol | 18559-94-9 | Other PhACs | 4-OHPB | 1137-42-4 | UV filter | Atrazine | 1912-24-9 | Triazine |
| Amitriptyline | Amitriptyline | 50-48-6 | Psychiatric drug and stimulant | 4MBC | 36861-47-9 | UV filter | Bifenthrin | 82657-04-3 | Pyrethroid |
| Amoxicillin | Amoxicillin | 26878-78-0 | Penicillin (antibiotic) | Benzyl salicylate | 118-58-1 | UV filter | Carbophenothion | 786-19-6 | Organophosphate pesticide |
| Ampicillin | Ampicillin | 69-53-4 | Penicillin (antibiotic) | Bisphenol Ab | 80-05-7 | Plasticizer | Chlorpyrifos | 2921-88-2 | Organophosphate pesticide |
| Atenolol | Atenolol | 29122-68-7 | β-blocker (antihypertensive) | Cashmeran | 33704-61-9 | Other fragrances | Cyfluthrin (I-IV) | 68359-37-5 | Pyrethroid |
| Atorvastatin | Atorvastatin | 134523-00-3 | Lipid regulator | Celestolide | 13171-00-1 | Polycyclic musk | Cypermethrin (I-IV) | 52315-07-8 | Pyrethroid |
| Azithromycin | Azithromycin | 83905-01-5 | Macrolide | DEET | 134-62-3 | Insect repellent | Deltamethrin | 52918-63-5 | Pyrethroid |
| Beazafibrate | Beazafibrate | 41859-67-0 | Lipid regulator | EHMC | 80334-59-7 | UV filter | Dieldrin | 60-57-1 | Organochlorine pesticide |
| Caffeine | Caffeine | 58-08-2 | Psychiatric drug and stimulant | Ethylhexyl salicylate | 118-60-5 | UV filter | Endosulfan Sulfate | 1031-07-8 | Organochlorine pesticide |
| Carbamazepine | Carbamazepine | 298-46-4 | Psychiatric drugs and stimulants | Exalreonone | 14359-54-1 | Macroyclic musk | Endrin | 72-20-8 | Organochlorine pesticide |
| Cefadroxil | Cefadroxil | 50370-12-2 | Cephalosporin | Hahalolide | 39402-57-3 | Macrocylic musk | Ethen | 563-12-2 | Organophosphate pesticide |
| Cefdinir | Cefdinir | 91832-40-5 | Cephalosporin | Helvotolide | 141773-73-3 | Other fragrances | Fenvalerate | 51630-58-1 | Pyrethroid |
| Cefquinome | Cefquinome | 84957-30-2 | Cephalosporin | Homosalate | 118-56-9 | UV filter | Heptachlor | 76-44-8 | Organochlorine pesticide |
| Cefotaxim | Cefotaxim | 80370-57-6 | Cephalosporin | IRGAROL | 28159-98-0 | Insect repellent | Heptachlor | 1024-57-3 | Organochlorine pesticide |
| Chloramphenicol | Chloramphenicol | 56-75-7 | Macroline | Mexenone | 1641-17-4 | UV filter | Lindane | 58-89-9 | Organochlorine pesticide |
| Chlorotetracycline | Chlorotetracycline | 57-62-5 | Tetracyclines | MTCS | 4640-01-1 | Antibacterial | Metoxycyclin | 72-43-5 | Organochlorine pesticide |
| Ciprofloxacin | Ciprofloxacin | 85721-33-1 | Quinolone (antibiotic) | Muscenone | 63314-79-4 | Macrocylic musk | o,p’-DDT | 789-02-6 | Organochlorine pesticide |
| Clarithromycin | Clarithromycin | 81103-11-9 | Macrolide | Musconene | 541-91-3 | Macrocylic musk | p,p’-DDT | 72-54-8 | Organochlorine pesticide |
| Clindamycin | Clindamycin | 18323-44-9 | Lincosamides (antibiotics) | Musk ambrette | 85-66-9 | Nitro musk | p,p’-DDE | 72-55-9 | Organochlorine pesticide |
### Table 3. Cont.

| Compounds | Use | Pharmaceuticals | CAS | PCPs | CAS | Use | Pesticides | CAS | Use |
|-----------|-----|-----------------|-----|------|-----|-----|------------|-----|-----|
| Clofibric acid 882-09-7 | Lipid regulator | Musk ketone | 81-14-1 | Nitro musks | Parathion | 56-38-2 | Organophosphate pesticide |
| Danofloxacin 112398-08-0 | Quinolone (antibiotic) | Musk moskene | 116-66-5 | Nitro musk | Permethrin LII | 52645-53-1 | Pyrethroid |
| diclofenac b 15307-86-5 | Analgesic/anti-inflammatory | Musk R1 | 3391-83-1 | Macroyclic musk | Phenofoxin LII | 26002-80-2 | Pyrethroid |
| Doxycycline 564-25-0 | Tetracyclines | Musk tibetene | 145-39-1 | Nitro musk | Promethion | 1610-18-0 | Triazine |
| Enrofloxacin 93106-60-6 | Quinolone (antibiotic) | Musk sylene | 81-15-2 | Nitro musk | Prometryn | 7287-19-6 | Triazine |
| Estrone b 53-16-7 | Estrogen | Nonylphenol a b | 84852-15-3 | Plasticizer | Propazine | 139-40-2 | Triazine |
| Famotidine 76824-35-6 | Histamine H2/receptor antagonists | OTNE | 54464-57-2 | Other fragrances | Simazine a | 122-34-9 | Triazine |
| Fenofibrate 49562-26-9 | Lipid regulator | Oxybenzone | 131-57-7 | UV filter | Simetryn | 1014-70-6 | Triazine |
| Fenoprofen 29679-58-1 | Analgesic/anti-inflammatory | Phantolide | 15323-35-0 | Polycyclic musk | Terbutylazine | 5915-41-3 | Triazine |
| Fluoxetine 10238-21-8 | Anti-diabetic medication | Hydrochlorothiazide | 59-93-5 | Diuretic | Tonalide b | 1506-02-1 | Polycyclic musks |
| Flumequine 424-25-6 | Quinolone (antibiotic) | Triclosan b | 3380-34-5 | Antibacterial | γ-chlordane | 5103-74-2 | Organochlorine pesticide |
| Furosemide 54-31-9 | Diuretic | Triclocarban | 101-20-2 | Antibacterial | α-endorosulfan | 959-98-8 | Organochlorine pesticide |
| Glibenclamide 71787-03-7 | Other PhACs | Metronidazole | 443-48-1 | Nitrimidazol (antibiotic) | Norfloxacin | 79-57-2 | Tetracyclines |
| Ibuprofen b 15687-27-1 | Analgesic/anti-inflammatory | Metronidazole | 71827-03-7 | Other antibiotics | Naloxone b | 22204-53-1 | Analgesic/anti-inflammatory |
| Indomethacine 53-86-1 | Analgesic/anti-inflammatory | Metoprolol | 51384-51-1 | β-blocker (antihypertensive) | Norfloxacin | 70458-96-7 | Quinolone (antibiotic) |
| Ivermectin 71827-03-7 | Other antibiotics | Methotrexate | 59-05-2 | Other PhACs | Ofloxacin | 82419-36-1 | Quinolone (antibiotic) |
| Ketoprofen 22071-15-4 | Analgesic/anti-inflammatory | Metronidazol | 443-48-1 | Nitrimidazol (antibiotic) | Oxytetracycline | 303-81-1 | Aminocoumarin antibiotic |
| Lincomycin 154-21-2 | Lincosamide (antibiotic) | Monensin | 17090-79-8 | Other antibiotics | Oxytetracycline | 22204-53-1 | Analgesic/anti-inflammatory |
| Mefenamic Acid 61-68-7 | Analgesic/anti-inflammatory | Nadolol | 15338-39-9 | β-blocker (antihypertensive) | Oxacillin | 66-79-5 | Penicillin (antibiotic) |
| Metoprolol 51384-51-1 | β-blocker (antihypertensive) | Naloxone b | 22204-53-1 | Analgesic/anti-inflammatory | Oxytetracycline | 70458-96-7 | Quinolone (antibiotic) |
| Methotrexate | 59-05-2 | Other PhACs | 959-98-8 | Organochlorine pesticide | Penicillin-G | 61-33-6 | Penicillin (antibiotic) |
Table 3. Cont.

| Compounds                      | CAS       | Use                  | OPFRs | CAS       | Use                  | PAHs      | CAS       | PCBs     | CAS       |
|--------------------------------|-----------|----------------------|-------|-----------|----------------------|-----------|-----------|----------|-----------|
| Phenazone                      | 60-80-0   | Phenazone type       |        | 126-73-8  | Flame retardant      | Acenaphthene | 83-32-9  | PCB28     | 7012-37-5 |
| Phenylbutazone                 | 50-33-9   | Phenazone type       |        | 115-86-6  | Flame retardant      | Acenaphthylene | 208-96-8 | PCB52     | 35693-99-3 |
| Pindolol                       | 13523-86-9| β-blocker (antihypertensive) |      | TBP-N     | Flame retardant      | Anthracene | 120-12-7 | PCB101    | 37680-73-2 |
| Pravastatin                    | 81093-37-0| Lipid regulator      |        | TPP b      |                      | Benzo [b] fluorenone | 205-99-2 | PCB138    | 35065-28-2 |
| Propanolol                     | 525-66-6  | β-blocker (antihypertensive) |      |            |                      | Benzo [k] fluorenone | 207-08-9 | PCB153    | 35065-27-1 |
| Ranitidine                     | 66357-35-5| Histamine H2/receptor antagonists |      |            |                      | Benzo[a] anthracene | 56-55-3  | PCB180    | 35065-29-3 |
| Rifampicin                     | 13292-46-1| Other antibiotics     |        |            |                      | Benzo[a] pyrene | 50-32-8  |           |          |
| Roxithromycin                  | 80214-83-1| Macrolide            |        |            |                      | Benzo[g,h,i] perylene | 191-24-2 |           |          |
| Salicylic Acid b              | 69-72-7   | Analgesic/anti-inflammatory |      |            |                      | Chrysene | 218-01-9 |           |          |
| Sparfloxacin                   | 110871-86-8| Quinolone (antibiotic) |      |            |                      | Dibenzo[a,h] anthracene | 53-70-3  |           |          |
| Sypramycin                     | 8025-81-8 | Macrolide            |        |            |                      | Fluoranthene | 206-44-0 |           |          |
| Sulfadiazine                   | 68-35-9   | Sulfonamide (antibiotic) |      |            |                      | Fluorene | 86-73-7  |           |          |
| Sulfadimethoxine               | 122-11-2  | Sulfonamide (antibiotic) |      |            |                      | Indeno[1,2,3-Cd] pyrene | 193-39-5 |           |          |
| Sulfaguanidine                 | 57-67-0   | Sulfonamide (antibiotic) |      |            |                      | Phenanthrene | 85-01-8  |           |          |
| Sulfamethazine                 | 57-68-1   | Sulfonamide (antibiotic) |      |            |                      | Pyrene | 129-00-0 |           |          |
| Sulfamethoxazole               | 144-82-1  | Sulfonamide (antibiotic) |      |            |                      |           |           |          |          |
| Sulfamethoxazole                | 723-46-6 | Sulfonamide (antibiotic) |      |            |                      |           |           |          |          |
| Sulfamethoxypyridazine         | 80-35-3   | Sulfonamide (antibiotic) |      |            |                      |           |           |          |          |
| Sulfanilamide                  | 63-74-1   | Sulfonamide (antibiotic) |      |            |                      |           |           |          |          |
| Sulfathiazole                  | 72-14-0   | Sulfonamide (antibiotic) |      |            |                      |           |           |          |          |
| Sulfisoxazole                  | 127-69-5  | Sulfonamide (antibiotic) |      |            |                      |           |           |          |          |
| Tetracycline                   | 60-54-8   | Tetracyclines        |        |            |                      |           |           |          |          |
| Tiamulin                       | 55297-95-5| Amphenicol           |        |            |                      |           |           |          |          |
| Timolol                        | 26839-75-8| β-blocker (antihypertensive) |      |            |                      |           |           |          |          |
| Trimethoprim                   | 738-70-5  | Dihydrofolate (antibiotic) |      |            |                      |           |           |          |          |
| Tysolos                        | 1401-69-0 | Macrolide            |        |            |                      |           |           |          |          |

a Priority pollutants or compounds for which Environmental Quality Standards in surface waters have been established [28]; b known or potential endocrine disruptor substances [1,29].
Figure 4. Compounds with a detection frequency in wells higher than 25% sorted by groups: polycyclic aromatic hydrocarbons (PAHs), pesticides, pharmaceutically active compounds (PhACs), personal care products (PCPs) and organophosphorus flame retardants (OPFRs).

Among the 63 detected compounds, antibiotics, the pesticide terbuthylazine, the PCP triclosan and the PAH acenaphthene were selected for discussion. The selection was based on results from previous studies, use of the compounds, frequency of detection, persistence in aquatic media and environmental risk.

4.3. Antibiotics

Most antibiotics were detected in the lower sub-basin (sector A; Figure 5). Among them, sulfamethoxazole was one of the most frequently detected. It is one of the sulfonamides found in the basin, which is a group of antibiotics commonly used in both veterinary and human medicine [30]. Sulfamethoxazole was detected in 50%, 22% and 25% of the groundwater samples of sectors A, B and C, respectively. In groundwater, the highest concentration was registered at point G26 (29.1 ng/L), whereas the highest values in surface waters were recorded in the river mouth, S27 (128 ng/L), and at the head of the Guadalteba River (S15: 56.2 ng/L).

Figure 5. Frequency of detection of antibiotics in groundwater in sectors A, B and C.

In a study conducted with the aim of assessing the environmental factors on groundwater antibiotic occurrence, Menció and Mas-Pla [16] observed that antibiotic spatial distribution was statistically more
related to groundwater properties than to parameters linked to potential sources, although solute transport parameters remained essential in order to fully explain antibiotic spatial distribution.

Sulfonamides are ampholitic compounds and sulfamethoxazole dissociation constants are \( pK_{a,\text{acid}} = 1.6 \) and \( pK_{a,\text{base}} = 5.7 \) [30], which means that it is negatively charged under typical environmental pH conditions (\( pH \approx 7–9 \)). The pH values recorded in groundwater across the basin ranged from 7.03 to 9.13. Thus, these compounds can migrate easily due to repulsion from negatively charged surfaces of clays and organic matter. Furthermore, they have a low \( \log K_{\text{ow}} (−0.1 \text{ to } 1.7 \text{ [31]}) \), and therefore avoid hydrophobic sorption. Sulfamethoxazole has not been identified as either easily biodegradable or sensitive to photolysis under neutral and basic pH conditions [32]. Residues of sulfamethoxazole have also been found in other basins [33]. The persistence of this compound, along with its capability to avoid sorption, is potentially a reason for its wide distribution.

Despite the high frequency of detection in sector A, many potential point sources of antibiotics such as pig farms are mainly located in the northwestern part of the basin (sector C) whose waste waters, along with those from urban areas, enter the Venta River, the main stream in sector C that flows into the dam system in the center of the basin. The antibiotics distribution in the target areas presumably responds to two factors: the hydrogeological dynamics (modified by hydraulic infrastructures) of the basin and the use of pig manure as an organic fertilizer in agriculture.

The three dams situated in the center of the basin collect the surface water from the upper basin (sectors B and C) to fulfill water demand. The Guadalhorce River in sector B is hydraulically connected with the porous aquifer, whereas the Venta River, sector C, recharges the aquifers which finally drain through a spring outflowing into the dam. The surface water is eventually released downstream (towards sector A) through irrigation channels and to the Guadalhorce riverbed. The effect of surface water flowing from dams into the aquifer of the lower sub-basin (sector A) is reflected in Figure 6. An enrichment of the water isotopic composition (\( \delta^{2}H/\delta^{18}O \)) is observed in waters of sector A in comparison to waters from the upper basin.

![Figure 6. Relation of \( \delta^{2}H \) and \( \delta^{18}O \) (‰) of water molecules in monitored surface waters (SWs) and groundwater (GW) in the Guadalhorce River basin.](image)

Sampled groundwater with high concentrations of chloride showed higher values of \( \delta^{18}O \) (‰) (Figure 7). Accordingly, water used for irrigation infiltrates into the aquifer and is evaporated and salinized, and then it is pumped back to the surface and further reused.
Since some antibiotics are found in the upper and the lower basin (sulfadiazine, sulfamethoxazole, timethoprim, lincomycin and monensin), and since they are more frequently detected in the lower sub-basin where they also present a higher concentration (Figure 8), it can be assumed that possible antibiotic sources exist in both sub-basins; however, these chemicals tend to accumulate in sector A. This tendency is probably a consequence of groundwater–surface water exchange processes and of the hydraulic infrastructure that conducts surface water from the upper basin towards the lower basin aquifer through the dams and through irrigation (Figure 6). Irrigation returns (Figure 7) also potentially contribute to pollutant accumulation.

Pig manure used as fertilizer in agriculture is another potential antibiotics source. It is abundantly applied to crops during the spring and autumn in the northwestern area (sector C) and also in the lower part, along with chemical fertilizers for citrus crops [27]. Other potential sources include non-treated
urban waste water discharges into the water courses all along the basin. Small urban areas (mainly in the lower part) are not connected to sewer systems [17].

4.4. Pesticides. Terbuthylazine

The broad spectrum herbicide terbuthylazine was present in 85% of the groundwater samples of the basin with a concentration ranging from 2.21 ng/L to 5.73 ng/L. It was detected in 100% of groundwater samples in sector B, whereas in both sector A and C, it was found in 75% of the samples. It has already been identified as one of the most commonly found pesticides in the area [17]. Terbuthylazine is a very weak base ($pK_a = 2$). Thus, a non-ionic species exists over nearly the entire pH range and its sorption is dominated by hydrophobic partitioning to sorbent organic matter ($\log K_{ow} = 3.4$ [34]). In fact, its persistence has been partly attributed to the strong adsorption capacity on humic substances [35,36]. Consequently, transport via sediment and organic matter during water infiltration through an unsaturated zone is an important pathway towards groundwater [37].

In the Guadalhorce River basin, agriculture, with irrigated and rain-fed crops, is the anthropogenic activity affecting the largest area (more than 50% of the total area [27,38]). Irrigated agriculture is concentrated in the alluvial lands of the lower basin (sector A; mainly citrus crops) and in the central zone of the upper basin, in sector B (mainly herbaceous crops like wheat, barley, legumes or tubers). There are also four golf courses near the coast (sector A) and one near the town of Antequera (sector B), which possibly use fertilizers and pesticides as well for lawn maintenance.

4.5. Personal Care Products. Triclosan

The antimicrobial triclosan was detected in 85% of the groundwater samples in the basin, being more frequently detected in sector B (100%), and present in 75% of groundwater samples of sectors A and C. Triclosan presents an important hydrophobic adsorption potential ($\log K_{ow} = 4.76$ [39]), allowing for an efficient removal in WWTPs as it absorbs onto the sewage sludge. Consequently, one the most important sources of triclosan in the environment is the use of sewage sludge (biosolids) from WWTPs as a fertilizer for crops [40].

Both the use of biosolids as fertilizers and discharge of non-treated wastewater are possible sources in the Guadalhorce River basin [17]. Wastewater discharge is a direct input into surface water courses. Groundwater is potentially reached through application of reclaimed sewage sludge on agricultural land, thus leading to a widespread presence of the pollutant in the basin.

4.6. Polycyclic Aromatic Hydrocarbons. Acenaphthene

Acenaphthene was the only PAH detected with a significant frequency (Figure 4). It was found in 38% of total groundwater samples of the basin. It is mainly present in the lower part of the basin (sector A), being detected in 87% of the samples collected in this area. Acenaphthene concentration ranged from 0.66 mg/L (G30) to 0.84 mg/L (G31).

Low molecular weight PAHs (with two to three benzene rings), such as acenaphthene, are normally released during petroleum processing, whereas high molecular weight PAHs are considered to originate from combustion [41,42]. Petroleum-related activities such as gas stations and gas and oil pipelines exist in the Guadalhorce River basin (Figure 9). The Arahal-Málagas oil pipeline and the Puente Genil-Málagas gas pipeline traverse the basin from NW–SE and N–S, respectively [17]. Furthermore, the Puerto Llano-Málagas oil pipeline, currently out of service, traverses the basin along the left side of the lower part of the river [43]. Leaching from one of these sources in sector A should not be disregarded.
Figure 9. Hydrocarbon potential sources [17,43] in Guadalhorce River basin and the three target areas (A, B and C) with the sampling points.

5. Conclusions

A first description of the occurrence and distribution of a wide range of regulated pollutants and contaminants of emerging concern in the Guadalhorce River basin has been drawn up. The results show the occurrence of 63 organic contaminants in surface and groundwater, 21 of which were found at least in 25% of the groundwater samples. Seventeen compounds were detected per groundwater sampling point, on average. The maximum number of contaminants was detected in a well situated near the river mouth (55 compounds), reflecting a strong influence on water quality from pollutant sources in this area, such as the discharge of treated and non-treated urban waste waters from urban areas and industrial sites.

Twenty-two different antibiotics have been found in water samples. Possible sources are waste water discharge into surface waters from urban areas and from intensive livestock production sites, which are especially numerous in the northwestern part of the basin. However, antibiotics spatial distribution does not show a correlation with the location of these potential sources. A possible tendency for antibiotics accumulation in the lower part of the basin is potentially attributed to surface–groundwater interactions and dynamics, which are modified by hydraulic infrastructures (dam system and irrigation channels).

On the contrary, the distribution of highly frequently detected triclosan and terbutylazine does not reflect a relation with water flow pathways, as they show a widespread distribution throughout the basin. The distribution difference with relation to antibiotics is attributed to the way these contaminants are potentially released into the environment, as well as their hydrophobicity. The herbicide terbuthylazine can derive from agriculture practices and the antimicrobial triclosan can derive from untreated urban wastewater discharges but also from the use of reclaimed sewage sludge as crop fertilizer.
The sorption of these compounds is dominated by hydrophobic partitioning to sorbent organic matter. Presumably, they remain in the soil where they are added and slowly reach groundwater during water infiltration through the unsaturated zone.

Extremely high concentrations of acenaphthene (polyaromatic hydrocarbon) have been measured in water samples from the lower part of the river basin, ranging from 0.66 mg/L to 0.84 mg/L. A possible leaching could be taking place from a petroleum-related activity or structure in this area.

It is known that full characterization and quantification in aquifer media and the fate of detected compounds is difficult and challenging and requires long-term monitoring to fully assess pollution exposure and to evaluate the response and correlation of analyzed organic chemicals to different hydrological factors, such as precipitation [12,44] and hydrochemical parameters [15,45].

Nevertheless, this is the first time an analysis and evaluation of such a great number of organic pollutants has been performed in this area. The obtained results yield important information for water resource management and provide a foundation for further research in the Guadalhorce River basin. Future monitoring practices and analyses can be optimized by focusing on selected contaminants and factors likely governing the distribution of the different pollutants. As observed, these factors can not only be the physico-chemical properties of the compounds, but also hydraulic infrastructures, which modify hydrogeological functioning of the basin and, thus, predetermine pollutant transportation and distribution.

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