Assessment of a wide array of contaminants of emerging concern in a Mediterranean water basin (Guadalhorce river, Spain): Motivations for an improvement of water management and pollutants surveillance

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HIGHLIGHTS

- Hydro(geo)logical data to understand CECs occurrence in water resources
- Most frequent pollutants are PCPs and flame retardants/plasticizers.
- Highest concentrations of fragrance galaxolide in water resources across Europe
- Correlation between hydrophilic pollutants and conservative ion chloride
- Management of water resources controls the increased presence of certain CECs.

GRAPHICAL ABSTRACT
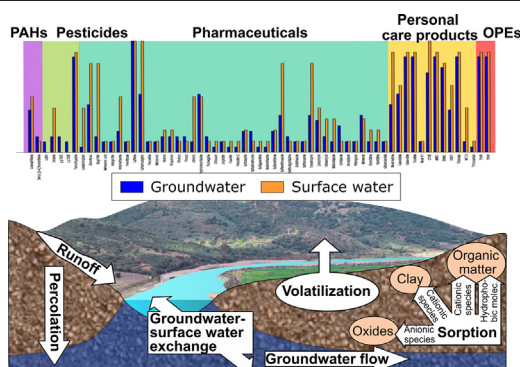
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ABSTRACT

This study investigates the occurrence and distribution of 185 organic contaminants (regulated pollutants and contaminants of emerging concern; CECs) in surface and groundwater of the Guadalhorce River basin (southern Spain) providing the most detailed dataset regarding organic pollution presented so far in this area. Up to 63 contaminants were detected in a monitoring campaign conducted in March 2016. Most contaminants were detected more frequently in surface water where they generally present higher concentrations suggesting the prevalence of wastewater discharges into streams as the main pollutant sources. In general, hydrophobic CECs presented the highest frequencies of detection and concentrations, which can be a consequence of several factors: (1) hydrophobic compounds show a higher retardation factor, which result, along with a continuous contaminant input, in a widespread and homogeneous distribution. In contrast, hydrophilic contaminants are more easily transported by water flows towards the lower basin and potentially accumulate as driven by groundwater flow and because of low renewal rates in the detrital aquifers caused by re-pumping and irrigation return flows in agricultural lands; (2) hydrophobic CECs studied in this research are mainly personal care products and organophosphate esters flame retardants and plasticizers, which are present in many different products and are used in large amounts; Also, (3) use of biosolids (reclaimed sewer sludge) as fertilizer for crops is potentially an additional diffuse source of organic pollutants in the study area contributing to a widespread distribution, especially for hydrophobic compounds. Obtained results highlight the need to better define the potential risk of non-regulated contaminants in water resources as well as the great impact of untreated wastewater discharges.

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1. Introduction

For several decades, concern about anthropogenic organic pollutants has prompted international efforts to eliminate or control their use and disposal. Nonetheless, pollutants subjected to regulatory control in water bodies are only a small fraction of the total of chemicals commercially available and potentially released into the environment (Daughton, 2004). Non-regulated pollutants are known as "emerging pollutants" or "contaminants of emerging concern" (CECs), whose ubiquitous presence has been recently recognized as a health and ecological problem (Lapworth et al., 2012). Important groups of CECs are Pharmaceutical Active Compounds (PhACs), Personal Care Products (PCPs), and organophosphorus compounds, a new alternative to brominated flame retardants and plasticizers.

As shown by an increasing research domain, CECs potentially entail hazards for ecosystems and human health such as bioaccumulation (Moreno-González et al., 2016) and biomagnification, endocrine disruption (Gago-Ferrero et al., 2012; Demeneix and Slama, 2019), antibiotic-resistant bacteria proliferation (Thai et al., 2018; Zainab et al., 2020) and toxicity (López-Pacheco et al., 2019), which can also be promoted by a "cocktail effect" (Pomati et al., 2008).

Most important sources are treated and untreated wastewaters from urban areas and industrial sites (Teijon et al., 2010; Gogoi et al., 2018) into streams. Thus, it is essential to determine the hydrological and hydrogeological functioning of the study area when studying the distribution of organic contaminants at a field scale. Other sources include waste disposal from livestock production sites (Ghirardini et al., 2020) and application of reclaimed sewage sludge (biosolids) as fertilizer (Yang and Metcalfe, 2006; Clarke and Smith, 2011).

Several processes influence pollutants fate in the environment and depend upon both their physicochemical properties and environmental characteristics. Chemicals infiltrating through soil are subjected to sorption mostly depending on the molecule speciation, hydrophobicity and field pH (Schaffer and Licha, 2015). Loss mechanisms for many organic pollutants are photodegradation in surface waters (especially for PhACs) and aerobic biodegradation (Baena-Nogueras et al., 2017), although less successful biodegradation is expected in groundwater if aerobic conditions are limited (Watanabe et al., 2010). Nonetheless, a continual presence of many CECs in aquatic environments is rather attributed to a constant release through sewage discharges, regardless of environmental half-life (Daughton, 2004). Transport in the atmosphere as gas or aerosol is also possible for many organic compounds (Wania and Mackay, 1996), including CECs such as organophosphate esters (OPEs) flame retardants and plasticizers (Castro-Jiménez et al., 2014) and synthetic musks (Peck and Hornbuckle, 2006; Villa et al., 2014).

The main goal of this study was to investigate the occurrence and spatial distribution of 185 regulated and non-regulated organic contaminants in groundwater and surface water of the highly anthropized Guadalhorce River basin (southern Spain). Investigated contaminant groups were: polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pesticides, PCPs, PhACs and OPEs. To clarify, when the term *CECs* is used in this text, reference is only made to PCPs, PhACs and OPEs. PCBs, PAHs and pesticides are *regulated pollutants*.

This is the first time an analysis and evaluation of such a great number of organic pollutants is performed in this area. The objectives were 1) to provide a snapshot of the situation of the basin regarding water pollution by organic chemicals and 2) to identify the main processes governing the distribution of pollutants taking into account the presence of potential sources, the hydrological and hydrogeological context of the studied river basin and water resources management along with the main physico-chemical characteristics of the target contaminants, yet while being aware of the difficulty of the task given the wide variety of factors involved. By doing so, potential flaws of land or water management can be pointed out and management improvements can be addressed.

The occurrence of anthropogenic organic pollutants in surface and groundwater has been investigated from the regional hydrogeological perspective by several authors (Teijon et al., 2010; Estevez et al., 2016; Li et al., 2017; Boy-Roura et al., 2018, among others). While many of them consider a single aquifer or water system, the study presented here considers a large area containing three different groundwater systems and approaches the interaction between them, which takes place through the hydrological system (modified by hydraulic infrastructure). Published work about CECs in groundwater at a large-scale is still considered to be limited (Bunting et al., 2021).

2. Study area

The Guadalhorce River basin (3175 km^2) is located in the south of the Iberian Peninsula (Spain). The river (166 km length) rises in the northeast of the basin and it flows into the Mediterranean Sea, to the southwest of the city of Malaga (Fig. 1). Temperatures annual mean value ranges from 13 °C to 18 °C. The wet season, with frequent extreme rainfall events, last from October to February and the driest season last from June to September. Rainfall values vary from less than 400 mm/year and 1100 mm/year in mountainous areas. From a practical point of view, the Guadalhorce river basin is divided in two sections (Fig. 1): the northern sub-basin whose flatlands are located at higher altitude (300–600 m a.s.l.), and the southern sub-basin (0–200 m a.s.l. for the altitude of its flatlands; Sánchez-García, 2010). The hydrological functioning of the lower sub-basin is influenced by three dams collecting water from the upper basin.

There are three main aquifer types in the basin: calcareous, detrital and evaporitic. Carbonate aquifers springs feed the main surface watercourses. These 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 it contains greywackers and phyllites (shales) with disseminated pyrite and organic matter (Sánchez-García, 2010).

The only evaporitic aquifer is in the northern sub-basin and comprises Triassic outcrops of clays, sandstones and evaporative materials (gypsum and halite; Sánchez-García, 2010). These materials constitute as well the basement of the detritic and carbonate aquifers of the basin.

Detrital aquifers form the target areas of this research. These three water systems (referred to as *groundwater bodies* by the basin administration) are situated in the flatlands of the basin: the Lower Guadalhorce (sector A; Fig. 1), located in the lower part of the basin, and Vega de Antequera-Archidona (sector B; Fig. 1) and Teba-Almargen-Campillos area (sector C; Fig. 1), both of them located in the upper sub-basin.

Porous unconfined aquifer in sector A is formed by alluvial sediments (Quaternary): gravels, sands, silts and clays. The underlying rocks are Upper Miocene calcareous sandstones and conglomerates, and Pliocene conglomerates, marl and sand layers. Pliocene sediments thickness can reach 300 m and at the bottom of the series, conglomerates form a discontinuous confine aquifer, which lay underneath the marls. At a shallower level, interrupted sand layers formed semiconfined aquifer (Linares et al., 1995).

Porous unconfined aquifer in sector B is constituted by Neogene and Quaternary deposits such as calcareous sandstones and alluvial sediments (Carrasco-Cantos, 1986).

Two detritic aquifers and one carbonate that are hydrologically connected constitute the third target area (sector C). The detritic aquifers are constituted by calcarenites, conglomerates and marls (Miocene) and detrital materials of fluvial origin (Quaternary) the carbonate aquifer is formed by Jurassic limestones (Carrasco-Cantos et al., 2007a).

2.1. Pressures

The Guadalhorce River basin is heavily regulated by hydraulic infrastructures (dam system, irrigation channels and dykes to divert surface
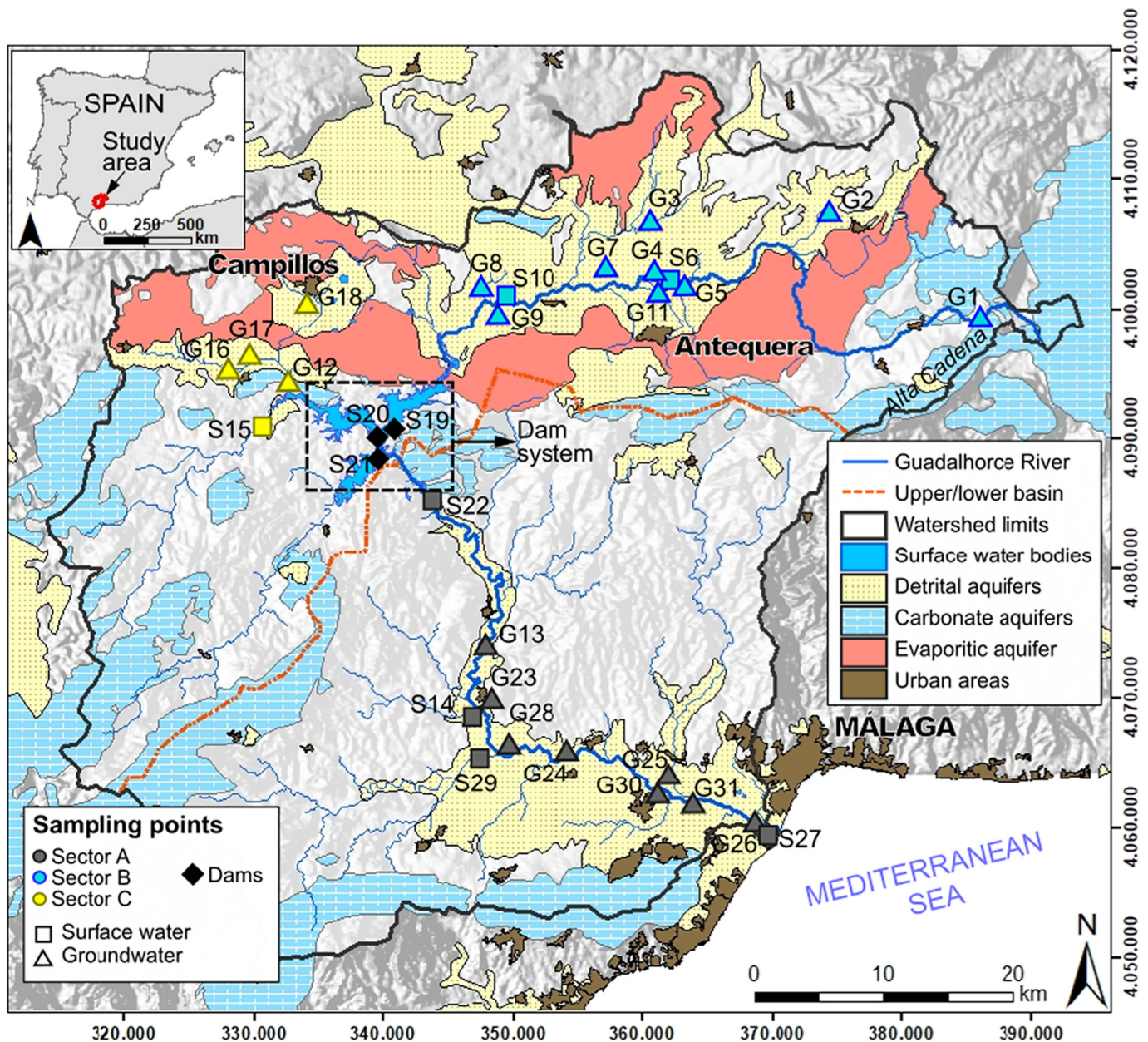
Fig. 1. The Guadalhorce river basin, the three target areas (sector A, B and C; indicated by the color of the sampling points symbol) and location of sampling points.

water resources) and gathers numerous anthropogenic activities constituting point and non-point (diffuse) pollution sources (Fig. 2).

The largest part of the area is used for agriculture (more than 50% of the total area). Irrigated agriculture is concentrated in the alluvial lands of the lower basin (sector A) and in the central zone of the upper basin (sector B). Intensive livestock production sites (mainly swine farms) are mostly located in sector C.

Most of the population concentrates in Málaga city: around 600,000 inhabitants out of the 900,000 inhabitants for the entire region (BOJA, 2013). Surface waters are regulated by reservoirs and dams to control flooding and to guarantee water supply in case of drought. Water demand in the river basin (340 hm^3/year) is fulfilled by aquifer exploitation and stored surface water. Most of this volume (75%) is consumed by agriculture (BOJA, 2013).

Discharges of non-treated wastewater are frequent since several urban areas lack wastewater treatment plant (WWTP). Although most neighborhoods or main urban areas suburbs have sewerage systems, many of them lack WWTP. Most rural scattered homes discharge

wastewater without any treatment through cesspits (Sánchez-García, 2010). Wastewater from Malaga city is treated although other important urban areas in sector A (with a population of around 60,000 inhabitants) lack WWTP (BOJA, 2013). It is estimated that two urban areas located in the lower part of sector A discharge 5.9 hm^3/year of untreated wastewater into the Guadalhorce River.

3. Materials and methods

This sampling campaign (March 2016) consisted of the collection of 31 groundwater and surface water samples (Fig. 1). Most groundwater samples belonged to detrital aquifers and were collected from private irrigation wells (<40 m deep) after continuous pumping. Sampling points G1 and G12 are springs draining carbonate aquifers and outflowing into the main water courses.

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
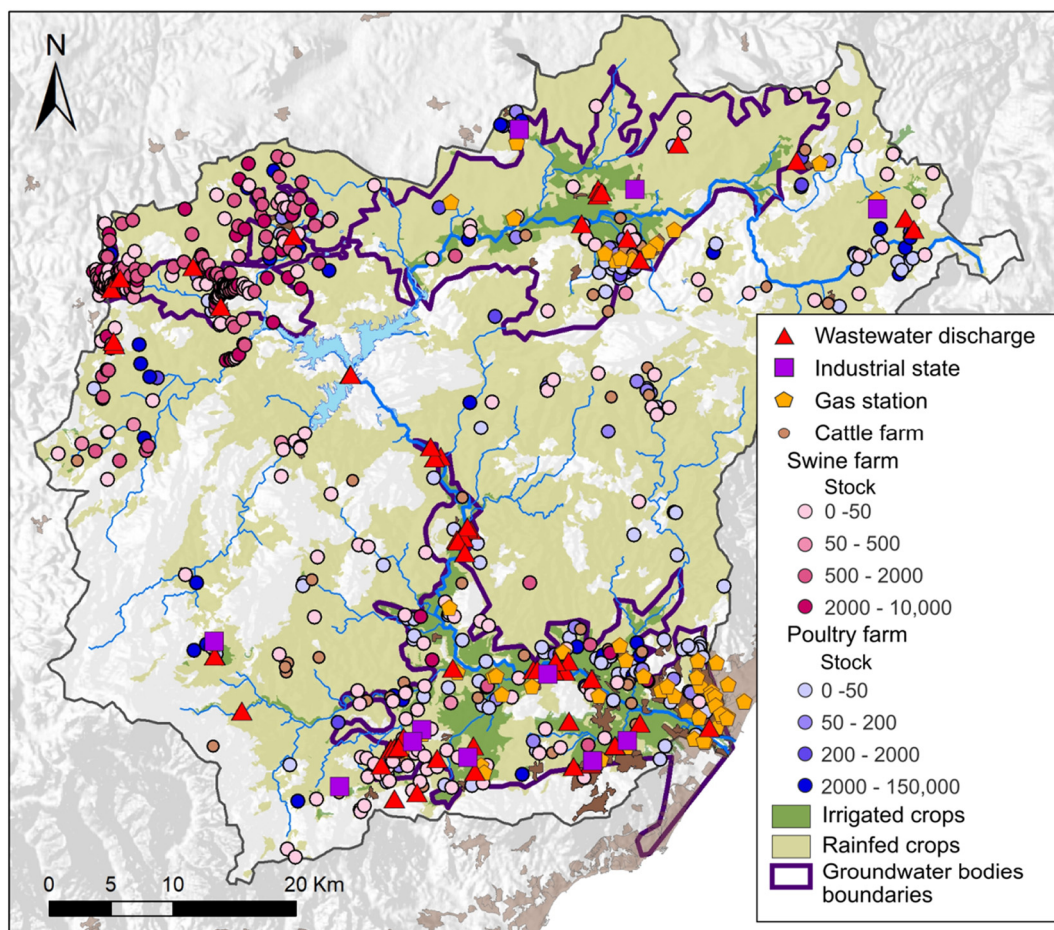
Fig. 2. Main point and diffuse pollution sources in the Guadalhorce River basin and groundwater bodies boundaries established for management purposes by the basin administration (Sánchez-García, 2010; BOJA, 2013).

bottles (120 mL) sealed with inverted cone caps; samples for organic compounds were stored in sterile amber glass bottles (1 L) with Teflon caps. All bottles were rinsed before sampling, carried in a cool-box and stored in a fridge (<4 °C) until analysis, generally performed within 24 h after sampling. A portable multi-parameter probe (Hach-Lange HQ40d; Hach, Loveland, CO, USA) was used to measure in situ physico-chemical parameters: pH, temperature, electrical conductivity (EC), redox potential (Eh) and dissolved oxygen (DO).

Major and minor water ions were determined with a Metrohm 881 Compact IC Pro (HPLC). δ^2H and $\delta^{18}O$ (‰; Vienna Standard Mean Oceanic Water), were determined in a Picarro Water Isotope Analyzer L2120i (laser spectroscopy). Hydrochemical and isotope analysis were conducted at the laboratory of the Center of Hydrogeology of the University of Malaga.

Samples were analyzed for 185 organic contaminants. PhACs were determined by solid-phase extraction followed by ultra-performance liquid chromatography–triple quadrupole mass spectrometry using a Bruker EVOQ Elite system (Bruker, Billerica, MA, USA) equipped with an electrospray ionization source (Baena-Nogueras et al., 2016). Regarding PCPs, PAHs, PCBs and OPEs and pesticides, analysis was performed using stir bar sorptive extraction (Pintado-Herrera et al., 2014) followed by gas chromatography (SCION 456-GC, Bruker) coupled to triple quadrupole mass spectrometry (SCION TQ from Bruker with CP 8400 Autosampler) (Pintado-Herrera et al., 2016). List of analyzed organic compounds and more information about the analytical methods for organic compounds is available in Supplementary material (Table S1).

4. Results

4.1. Surface and groundwater hydrochemical characteristics and isotopic composition

Hydrochemical and physico-chemical data of monitored surface and groundwater is available in Supplementary material (Tables S2 and S3). Influence from the evaporitic basement is reflected by SO_4^{2-}-Ca^{2+} facies in sector B (Fig. S1). By the same token, high sulfate concentrations (mean value of 786.9 ± 823.2 mg/L) and high EC values (mean value of 2640 ± 777 μS/cm) were observed in groundwater in this sector. Groundwater samples in sector A and C also revealed high values of sulfate (mean values of 169.3 ± 55.3 mg/L and 242.3 ± 265.3 mg/L, respectively). Although the evaporitic basement from the upper basin contributes greatly to the dissolved sulfate water content, a significant part is due to fertilizer application, especially in the lower basin (Urresti-Estala et al., 2015).

Surface water in dam S19 shows Cl^--Na^+ facies (Fig. S1) because of the saline spring contribution from the evaporitic aquifer (Carrasco-Cantos et al., 2007b). Cl^--Na^+ facies suggest seawater influence for water samples located near the river mouth. Mixed facies reflect that water composition from sector A and C result from different processes: rock-water interaction and water chemistry alteration by anthropogenic activities. HCO_3^--Ca^{2+} facies are associated to carbonate aquifers springs (G1, G12) and their contribution.

The threshold value for nitrates in groundwater (50 mg/L; European Parliament and the Council of the European Union, 2006) is exceeded in

all target areas (Table S3). In the upper sub-basin nitrate concentration occurs by mineral fertilizers application but in the western part (sector C) nitrate presence is from manure (Urresti-Estala et al., 2015), due to intensive pig farming (Fig. 2) and pig slurry irrigation.

Water stable isotope composition $\delta^{18}O$ and δ^2H (‰) broadly reflects the hydrological and hydrogeological dynamics in the basin (Fig. 3). Water from the upper basin (sector B and C) is generally more depleted in oxygen-18 and deuterium. An evaporation water line is formed by water samples from sector B, which is potentially attributed to irrigation return flows (Vadillo-Pérez et al., 2019). Surface water from the upper basin is collected in the dams before being released downstream. Evaporation during dam storage generates an oxygen-18 and deuterium enrichment revealing an end-member that act as a surface and groundwater source in sector A. In the lower basin water from dams is released through channels for agricultural irrigation and infiltrates in the aquifer in sector A. Sampled point S27 (surface water point located in the river mouth) is much more enriched in ^{18}O and ^2H as it is influenced by sea water.

4.2. Results of target organic pollutants according to group of classes

Results show that 63 out of 185 analyzed pollutants were found, at least once: two PAHs, five pesticides, 42 PhACs (among which, 22 antibiotics), 12 PCPs and two OPEs. PCPs and OPEs were the most frequently detected groups of pollutants. Fig. 4 presents all detected organic compounds and their frequency of detection in groundwater and surface water.

Concentrations of organic compounds were very variable ranging from concentration values under limits of quantification to over 0.8 mg/L for acenaphthene (PAH; Llamas et al., 2020). Minimum, maximum and mean values of organic pollutants concentrations are available in Supplementary material (Table S4). To calculate descriptive values, sampling point S14 was discarded. It was collected in a river section receiving important inputs of untreated urban wastewater and with a low river flow, thus limiting dilution. This sampling point is considered to represent raw wastewater effluents rather than fresh surface water.

41 out of 63 detected compounds were found more often in surface waters than in groundwater and maximum concentrations of detected compounds are generally lower in groundwater (Fig. 5). This is the case for all detected PhACs. This can be a consequence of a natural attenuation of aquifers (Jurado et al., 2012) as well as a reflection of the prevalence of wastewater discharges into streams as main CECs source (Lapworth et al., 2012). On the contrary, pesticides lindane and terbuthylazine revealed higher concentrations in groundwater, likely because pesticides are applied to agricultural lands and reach groundwater directly by infiltration through soil. Total concentration of pollutants regarding groups of classes (Fig. 6) is also generally higher in monitored surface water than groundwater, except for pesticides.

Terbuthylazine was the most frequently found pesticide being present in 86% and 90% of groundwater and surface water samples, respectively, but always under the European threshold value set for individual pesticides in groundwater (100 ng/L; 2006/118/EC). The priority substances benzo[*b*]fluoranthene, benzo[*k*]fluoranthene (PAHs) and the isomer γ of hexachlorocyclohexane (lindane) were detected also under the Environmental Quality Standards (European Parliament and the Council of the European Union, 2013) set for these substances in surface waters. Pesticides aldrin, p,p′DDD and p,p′DDE were detected only in groundwater. DDD and DDE occur as impurities in DDT and also as products of natural DDT transformation. Use and production of aldrin and DDT are banned in Europe (European Parliament and Council of the European Union, 2019). Therefore, occurrence of these substances might be due to ancient use and their high hydrophobicity and persistence rather than current use. On the contrary, lindane was found in both surface and groundwater which could indicate current application to soils and that lindane excess reaches surface waters.

Antibiotics sulfamethoxazole and trimethoprim, recently included in Watch list (Decision (EU) 2020/1161; European Commission, 2020), were both registered in 33% of groundwater samples and in 80% of surface water samples.

4.2.1. Pharmaceutical active compounds (PhACs)

Most frequently detected PhACs (over 50% of frequency of detection in groundwater or surface water) were caffeine (stimulant), carbamazepine (antiepileptic), ibuprofen and diclofenac (analgesics), hydrochlorotiazide (diuretic) and sulfamethoxazole and trimethoprim (antibiotics). This is
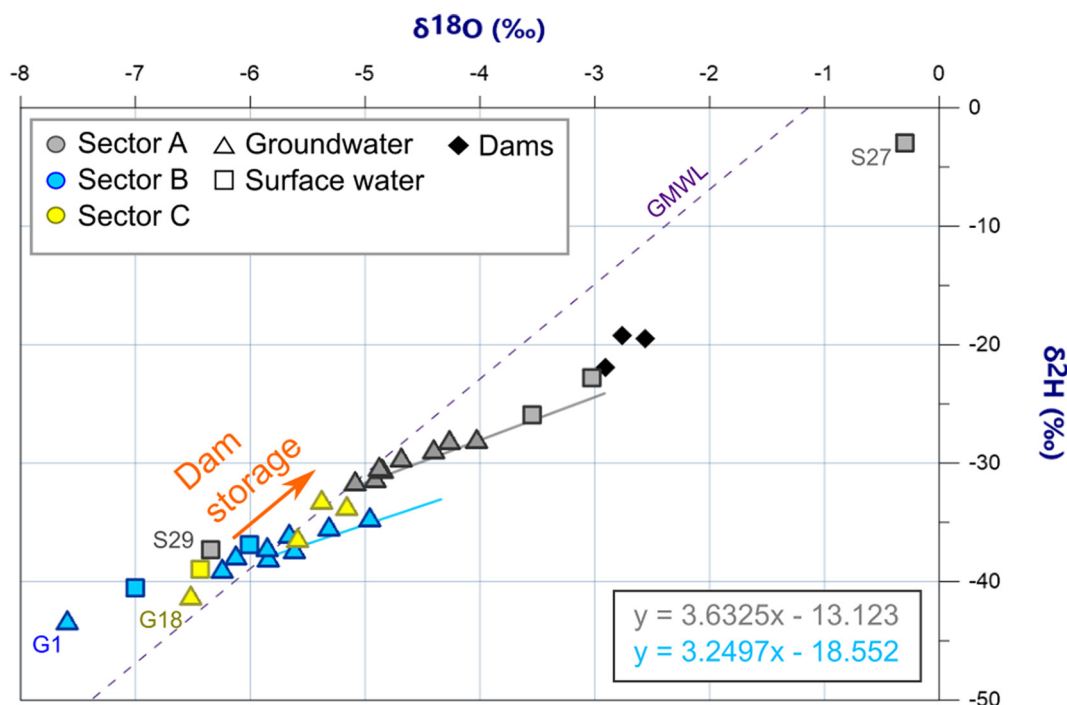

Fig. 3. Water stable isotopes ($\delta^{18}O$ and δ^2H, ‰) plot of monitored surface and groundwater in the three target areas (sector A, B and C) of the Guadalhorce River basin.
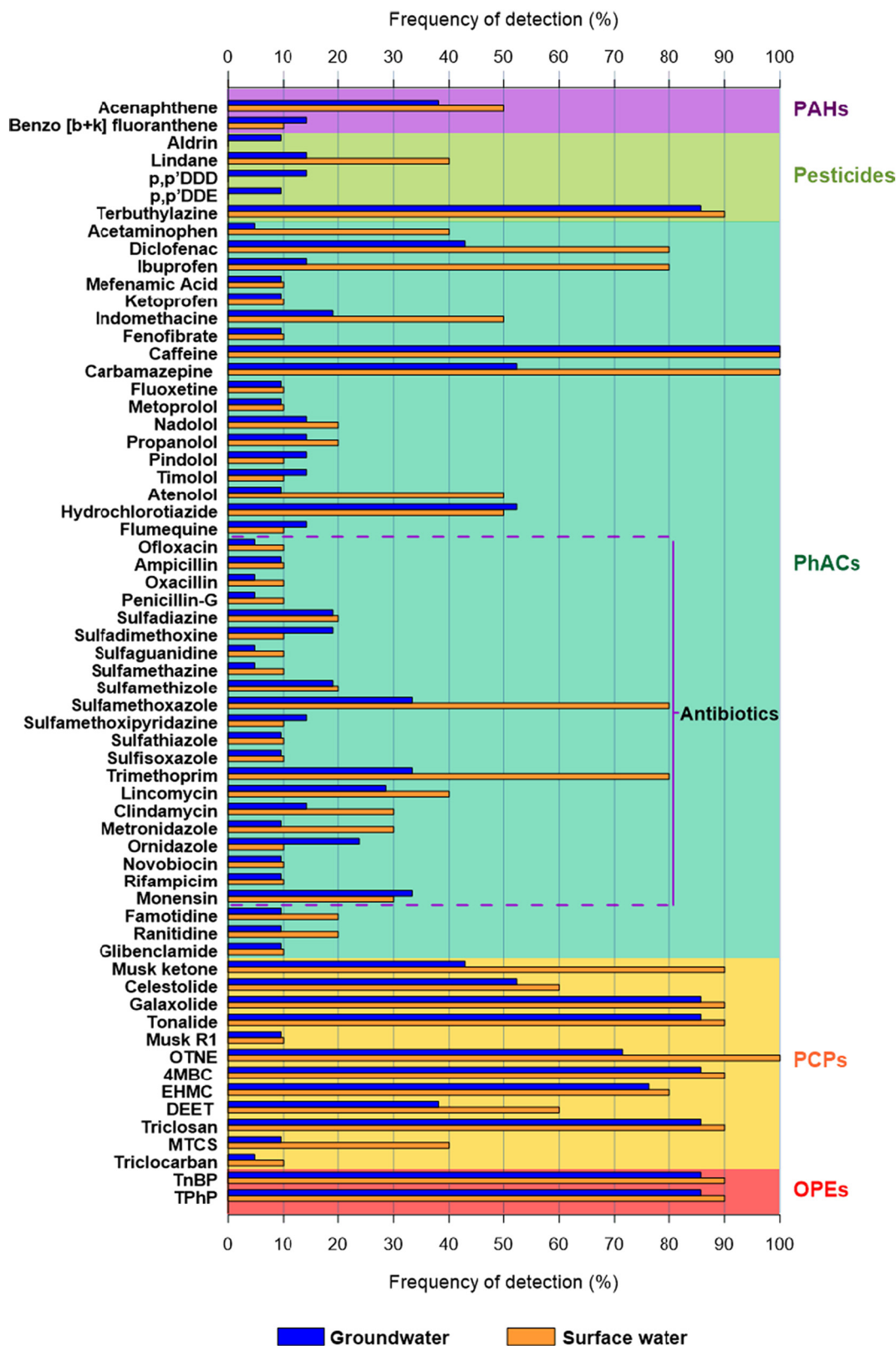
Fig. 4. Frequency of detection (%) of organic contaminants in surface and groundwater of the Guadalhorce River basin. Legend: PAHs: polycyclic aromatic hydrocarbons; PhACs: pharmaceutical active compounds; PCPs: personal care products; OPEs: organophosphate esters flame retardants and plasticizers.

consistent with results of other studies (Gros et al., 2007; Santos et al., 2007).

Caffeine, carbamazepine, hydrochlorothiazide and ibuprofen were on the list of chemicals produced in larger quantities (OECD, 2004).

Caffeine was present in all collected samples. Aside from being a highly consumed product, caffeine is both a weak acid and a weak base ($pk_{a,acid} = 14$ and $pk_{a,base} = 0.07$), which means that a neutral form is predominant at typical environmental pH values but it also
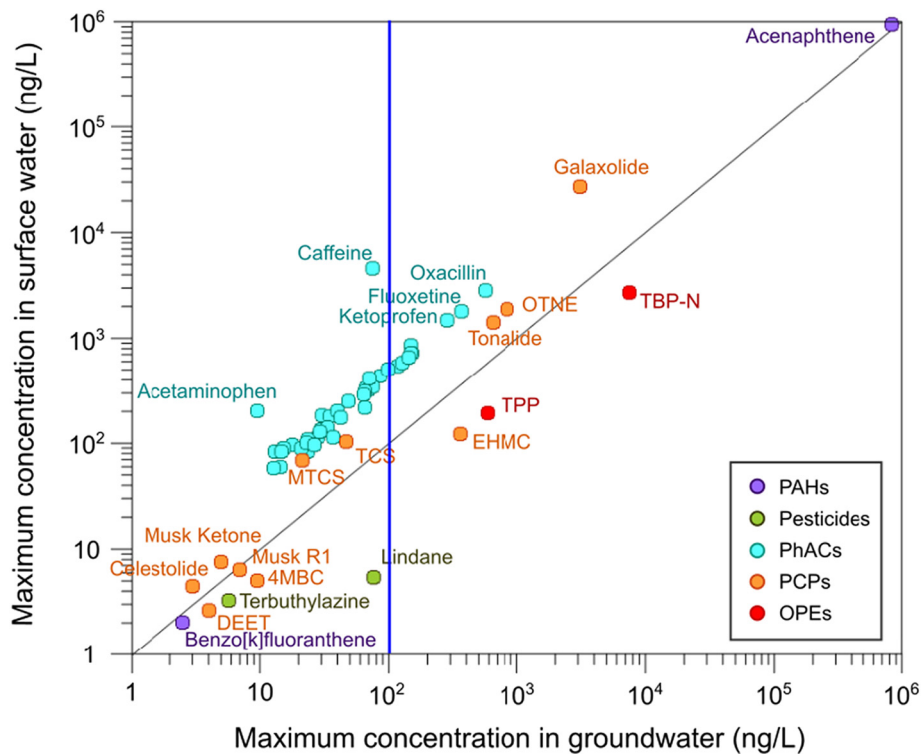
Fig. 5. Maximum concentrations of regulated pollutants and CECs detected in surface and groundwater in the Guadalhorce River basin. For comparison, vertical blue line is the EU limit for individual pesticides in groundwater (100 ng/L; European Parliament and Council of the European Union, 2006). Legend: same as in Fig. 4. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

presents a relatively low log k_{ow} (−0.07). Thus, it can be more present in the aqueous solution (Carere et al., 2012).

Carbamazepine, a very persistent pollutant with low removal rates in WWTP (Miao et al., 2005), was detected in 52% of groundwater samples and in all surface water samples.

Diclofenac was found in 43% of monitored groundwater and 80% of surface water. Hydrochlorothiazide was present in 52% of groundwater samples and it was present in 50% of surface water samples. High presence of these compounds can be due to a constant release from wastewater discharges as they are highly consumed compounds. Diclofenac is negatively charged under environmental conditions and thus it is hardly adsorbed in the subsurface (Biel-Maeso, 2018).

Antibiotics sulfamethoxazole and trimethoprim are commonly used combined to achieve synergistic effects (European Commission, 2020). Both are persistent in natural waters (Baena-Nogueras et al., 2017). Sulfamethoxazole is considered to migrate easily because of its hydrophilicity and negative charge under typical pH conditions (Avisar et al., 2009). Trimethoprim, is a weak base with $pk_{a,base} = 7.4$ (AlRabhiah et al., 2018). Registered pH values during the monitoring campaign were between 7.0 and 9.1. Hence, both neutral and positive species of trimethoprim would be present in the aqueous environment. Neutral form would considerably avoid sorption onto organic matter since this compound has a relatively low log K_{ow} value (0.91; Biel-Maeso, 2018).
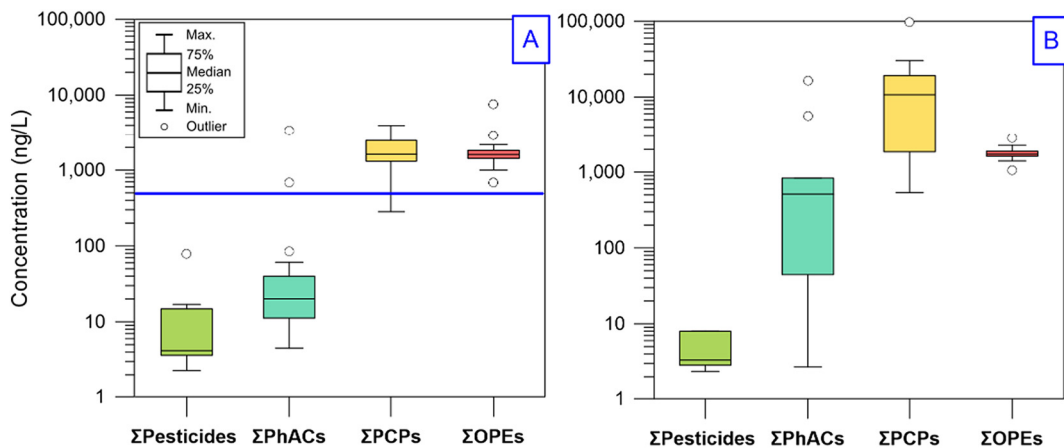
Fig. 6. Box-plot of total concentration of pesticides and CECs detected in groundwater (A) and surface water (B) in the Guadalhorce River basin. For comparison, horizontal blue line is the EU limit for total concentration of pesticides in groundwater (500 ng/L; European Parliament and Council of the European Union, 2006). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Mass-proportion of all antibiotics is plotted in a map in Fig. 7: the five most frequently detected antibiotics are represented with their own color whereas the sum of the concentration of the rest is represented under the label "other". It can be observed that sulfamethoxazole, sulfadiazine, trimethoprim, lincomycin and monensin are predominant in the upper sub-basin whereas in the lower part there is more variability, although these five antibiotics are still present. In the lower sub-basin, total concentration of antibiotics seems to increase in line with the flow direction suggesting an accumulation process.

4.2.2. Personal care products (PCPs)

Detected PCPs in monitored waters correspond to different subgroups (regarding type of use): DEET (insect repellent); 4MBC and EHMC (UV filters); triclocarban, triclosan and its metabolite: MTCS (antibacterials); musk ketone (nitro musk); celestolide, galaxolide and tonalide (polycyclic musks); musk R1 (macrocylic musk) and OTNE (other fragrances).

Most significant concentrations were registered for galaxolide (Fig. S2). Maximum concentration was detected in sampling point S14 (83,488 ng/L). This point of the river receives wastewaters discharges from urban areas lacking WWTP. As mentioned, this point has not been considered as representative of surface waters, but untreated wastewater effluents. Hence, concentration of galaxolide in surface water ranged from 890 to 26,990 ng/L with a mean value of 9587

ng/L. In groundwater, registered concentrations ranged from 435 to 3130 ng/L with a mean value of 1278 ng/L.

Synthetic musks are used as fragrances in many domestic and industrial products such as detergent, cosmetics, shampoo, perfume, etc. Nitro musks are being phased out because of their potential toxicity and environmental persistence and have been largely replaced by polycyclic musks. Among these, galaxolide and tonalide are used most often (Clarke and Smith, 2011).

In Spain, PCPs were reported by Teijon et al. (2010) in groundwater in the Llobregat aquifers where galaxolide was detected with a frequency of 98%, which is consistent with our results, and with a maximum concentration of 359 ng/L. In Europe, a maximum concentration of 23,000 ng/L in groundwater was also reported (Lapworth et al., 2012). In surface water, a maximum concentration of 12,500 ng/L for galaxolide was detected in a small and highly impacted brook in Berlin (Herberer et al., 1999).

4.2.3. Organophosphate esters (OPEs) flame retardants and plasticizers

OPEs flame retardants and plasticizers showed a widespread distribution in the river basin (Fig. 4). Both TnBP and TPhP were found in 86% of groundwater samples and in 90% of surface water samples. TnBP was detected in groundwater at a concentration ranging from 672 to 7503 ng/L (mean = 1818 ng/L) and in surface water with a concentration between 1166 and 2666 ng/L (mean = 1736 ng/L).
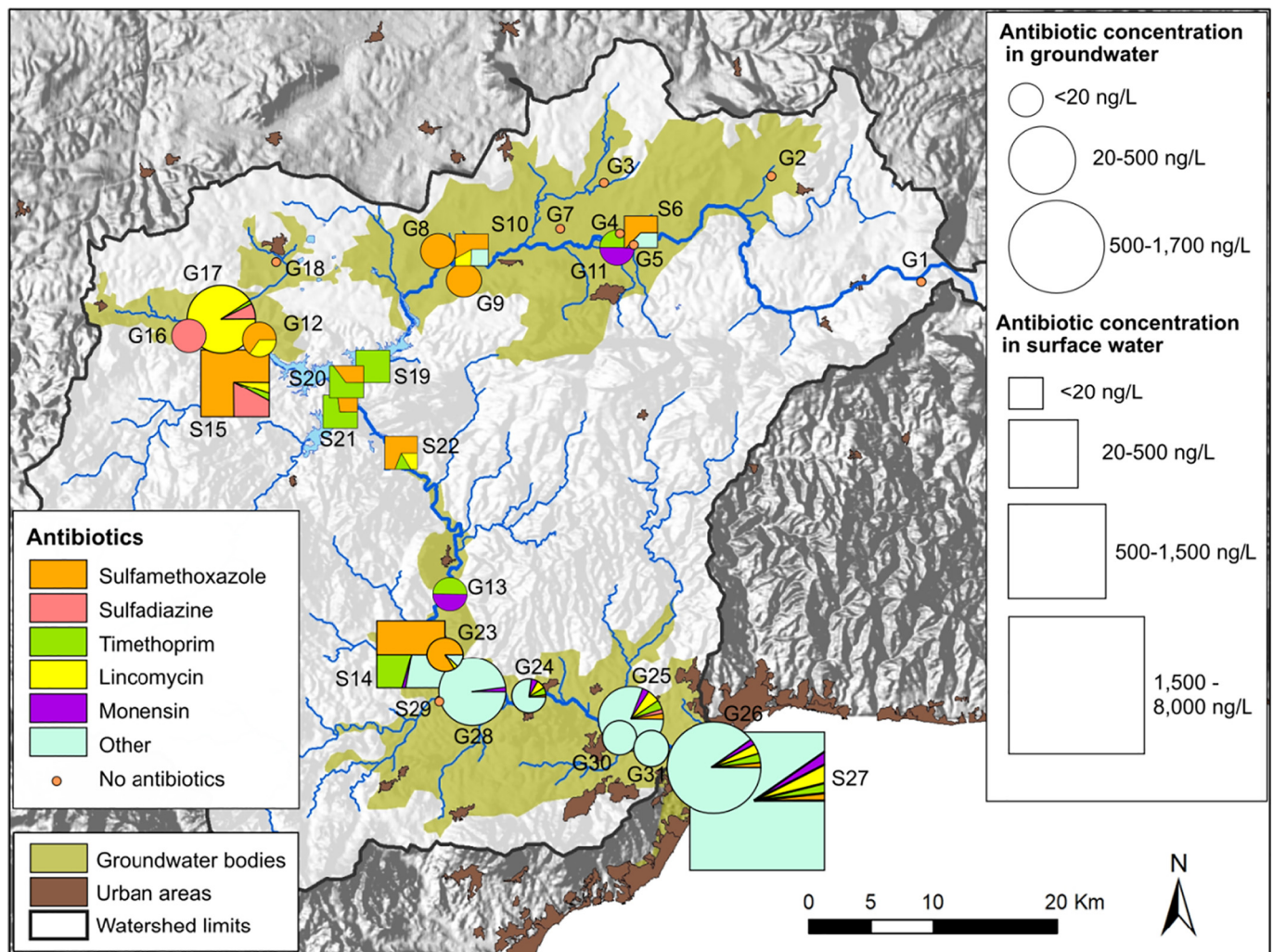

Fig. 7. Pie charts showing mass-proportion of detected antibiotics in monitored surface (squares) and groundwater (circles) in the Guadalhorce River basin. Note: label "Other" considers the rest of the 22 antibiotics detected. Total antibiotic concentration is indicated by size of circles and squares.

Concentration of TPhP in groundwater ranged from 8 to 588 ng/L (mean = 109 ng/L) and concentration in surface water ranged from 45 to 193 ng/L (mean = 93.0 ng/L).

Organophosphorus flame retardants have been proposed as alternatives to brominated flame retardants because of their toxicity and persistence, thus increasing the traded volume of the organophosphorus kind. Even so, TnBP and TPhP are mostly used as plasticizers and have many possible applications such as antifoam agent, hydraulic fluids, lacquers, plastic, solvent, electronic equipment, etc. (Van der Veen and de Boer, 2012). These compounds enter the aquatic environment mainly through hydraulic fluid leakages, by leaching and volatilization from plastics, and, to a minor extent, from manufacturing processes (Lassen and Lokke, 1999).

The maximum concentration levels reported for TPhP in river water is 7900 ng/L by the Danish Environmental Protection Agency (Lassen and Lokke, 1999). Fries and Püttmann (2001) registered TnBP concentrations up to 3716 ng/L in groundwater in Germany and a maximum concentration of 1510 ng/L in river water. Hence, the results of this study for TnBP are slightly higher than those found in literature.

5. Discussion

Obtained results reflect the ubiquity often attributed to anthropogenic organic pollutants. All water samples presented a content in organic pollutants, including sampling point G1 (Fig. S3), which is a spring draining a carbonate aquifer that is part of the Alta Cadena mountain range (Fig. 1). It is an unconfined aquifer whose water recharge origins from rain water infiltration through clefts and exokarstic forms on limestones and dolostones. The altitude of this range varies from 600 m a.s.l. at the edges to 1640 m a.s.l. (Mudarra and Andreo, 2007). Although direct pollution sources cannot be discarded in this area as a few anthropogenic pressures exist (e.g., campsite, mountain tourism, a road, grazing, a small cultivated area), pollution input through rainfall or atmospheric deposition should be considered. Some studies reported the presence of regulated and emerging pollutants in areas far from potential sources. Pesticide terbuthylazine, among other organic compounds, was detected in a glacial lake in Spanish Pyrenees (Santolaria et al., 2015) and in meltwater from Alpine glaciers along with other organic pollutants including polycyclic musks galaxolide and tonalide (Ferrario et al., 2017). Fries and Püttmann (2001) reported a concentration of up to 922 ng/L of TnBP in rain water, among other organophosphate compounds. Precipitation in the Alta Cadena mountain range take place essentially in winter and in springtime and they are linked to humid winds from the southwest (Mudarra and Andreo, 2007). Sector B gathers many anthropogenic activities (Fig. 2), including agriculture, intensive livestock production and industrial manufacturing such as a cosmetic factory situated near Antequera city, which can act as a pollutant atmospheric source (Chen et al., 2007). Fragrances volatilization from other sources such as landfills, WWTP and their receiving streams has also been suggested (Peck and Hornbuckle, 2006).

Generally, hydrophobic compounds showed a widespread distribution, in contrast to hydrophilic: most PCPs and OPEs are hydrophobic and most PhACs are hydrophilic (Table S4). In addition, total amount of hydrophobic CECs was greater than that of hydrophilic CECs (Fig. S4). Octanol-water partition coefficient of detected compounds is available in.

A greater frequency of detection of hydrophobic compounds can be due to several factors:

1) Hydrophobic compounds generally show higher retardation factor increasing travel time in the subsurface in contrast to hydrophilic compounds. Boy-Roura et al. (2018) also observed that antibiotics with predicted large retardation factors were the most frequently detected in the study area. Fig. 8 shows relations between conservative ion chloride and total amount of hydrophilic CECs (Fig. 8.1), total concentration of antibiotics (most of them are hydrophilic; Fig. 8.2),
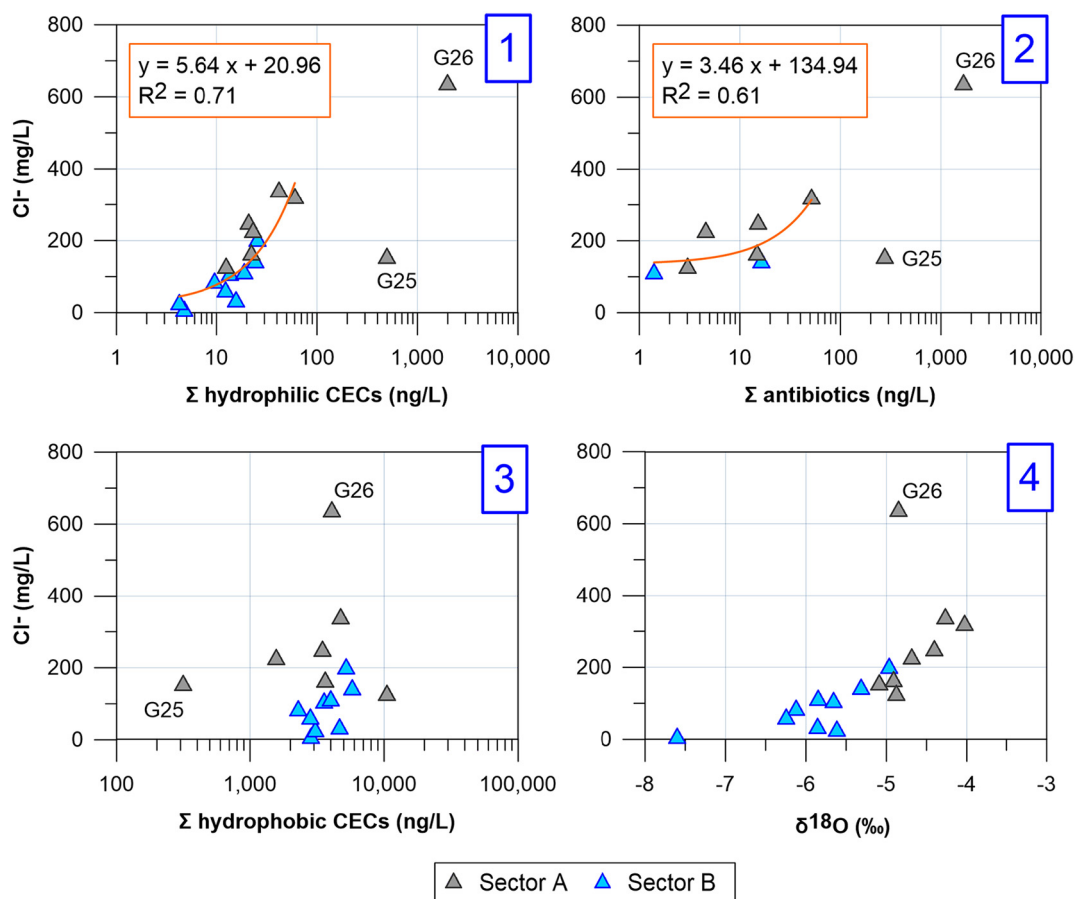
total concentration of hydrophobic compounds (Fig. 8.3) and $\delta^{18}O$ (Fig. 8.4) in monitored groundwater in sector A and B. It can be observed that there is no evident correlation between chloride and total concentration of hydrophobic CECs. On the contrary, hydrophilic compounds can be more easily transported by water flow as reflected by a slight correlation with chloride. Then, concentration of these compounds can be influenced by irrigation return flows that take place in sector A and B (Fig. 8.4) and thus accumulate. Low renewal rates due to re-pumping and irrigation return flows in agriculture lands (Urresti-Estala et al., 2016) also contribute to widespread high EC values (Table S2).

Correlation with chloride is also observed for total concentration of antibiotics. Given that most intensive livestock production sites are located in the northwestern part of the basin (sector C), a potential source of veterinary antibiotics has to be considered (Ghirardini et al., 2020) from this area. Wastewater from these facilities is often discharged into surface water courses. Surface water from the upper basin is collected in the dam system and eventually released downstream towards the Guadalhorce River bed but also towards irrigation channels leading water to agricultural lands in sector A. Hence, a transport of these antibiotics potentially takes place from surface water in the upper basin to groundwater in the lower part of the basin. This surface water-groundwater interaction is reflected in Fig. 3. This can be the reason why in the upper basin only a few types of antibiotics are detected, as they origin from similar anthropogenic activities (i.e. livestock farming), whereas in the lower basin there is more antibiotics variability (Fig. 7), as there is more heterogeneity regarding anthropogenic pollutants potential sources (Fig. 2).

Sampling points G25 and G26 were not considered to calculate trend line (Fig. 8.1 and .2) as they present characteristics that differ from the rest: G26 is the closest point to the coast so it presents a higher chloride concentration (potential seawater influence) and a very high level of organic pollutants since most population concentrates in the lowest part of the basin (BOJA, 2013); G25 is close to the Campanillas stream flowing from the NE potentially provoking salts dilution but organic pollutants input is still possible from the stream as anthropogenic activities are numerous in this area (Fig. 2). Total concentration of hydrophobic CECs, hydrophilic CECs and chloride concentration in groundwater are plotted according to main groundwater flow direction in Fig. 9. It can be observed that total content of hydrophilic CECs increases along flow direction in sector B (Fig. 9.B) whereas this is not evident for hydrophobic CECs. Effect of the tributary contribution near Antequera city is reflected by a slight chloride decrease as this stream originates from a carbonate aquifer. CECs increase at this same point can also be a consequence of the Antequera WWTP discharge.

In contrast, an accumulation process for hydrophilic CECs along groundwater flow is harder to observe in sector A. This is a more complex water system due to the presence of important wastewater inputs and river affluents. Correlation between chloride and hydrophilic CECs along the first kilometers throughout the aquifer can be due to an accumulation process along water flows, sharpened by re-pumping and irrigation returned flows. Fluctuations of these parameters in sector A can be also attributed to important loads of untreated wastewater into the river and tributaries contributions. Note that tributary contribution does not always involve both a decrease of chloride and CECs as shown by sampling point G25 (Fig. 9.A) and sampling points G4, G5 and G11 (Fig. 9.B) as anthropogenic pollution sources might still be present.

2) Hydrophobic compounds tend to absorb to sewage sludge during wastewater treatment (Clarke and Smith, 2011; Biel-Maeso et al., 2019) so their application to soils can entail a pollutants input such as for synthetic musks (Yang and Metcalfe, 2006). Since the 1990s, in Spain is regulated the use of reclaimed sewer sludge (biosolids) to fertilize agricultural lands (BOE, 1990), so in the Guadalhorce

Fig. 8. Bivariate correlation between conservative ion chloride with (1) total concentration of hydrophilic CECs, (2) total concentration of antibiotics, (3) total concentration of hydrophobic CECs and (4) $\delta^{18}O$ (‰) in monitored groundwater in sector A and B.

River basin this could be an additional diffuse source of CECs, especially of hydrophobic ones, thus contributing to a widespread distribution. However, this practice has just begun to be controlled by the water basin organization (BOJA, 2018) so little data about current patches receiving biosolids is available in this region. Nonetheless, one of the most worrisome issues about water pollution in this region is the general lack of wastewater treatment.

3) Hydrophobic CECs studied in this work are mostly PCPs and OPEs whereas hydrophilic compounds are mainly PhACs (Table S4). OPEs and PCPs are considered high production chemicals (Chokwe et al., 2020; Van der Veen and de Boer, 2012; Villa et al., 2014). High volume produced and consumed of these chemicals, in relationship with PhACs, might explain why studied compounds have been detected in such different amounts (Fig. S4). For comparison, production of galaxolide in Europe was about 1427 tons/year (OSPAR Commission, n.d.) whereas total consumption of diclofenac in Europe was estimated to be 179.8 tons/year (Lonappan et al., 2016). Additionally, use of galaxolide is estimated to be over seven times higher in Southern Europe than in Northern EU countries, with a general greater consumption of polycyclic musks in these countries (ECB, 2008).

6. Conclusions

The presented study yields the most complete dataset of organic pollutants occurrence in water resources in the Guadalhorce River basin presented so far. Thus, most analyzed contaminants have been investigated for the first time in this area.

PCPs and OPEs flame retardants and plasticizers were the most significant groups of pollutants in terms of frequency of detection and concentration. To the best of our knowledge no comparable concentrations have been reported for surface or groundwater. Most studies regarding CECs in groundwater conducted in Europe include pharmaceuticals as target contaminants which may distract from other compounds that are screened less regularly (Bunting et al., 2021). This work evinces that more attention has to be paid to other groups of CECs, notably PCPs and OPEs.

Many detected CECs showed concentrations above the EU limits set for pesticides in groundwater, highlighting the need to establish levels of risks that these substances may entail in the environment.

As discussed, high frequency of detection and high concentration of CECs (i.e. PCPs, OPEs and few PhACs) are potentially a consequence of different factors. Hydrophobicity of most frequently detected pollutants complicates their dragging by groundwater flows (larger retardation) which contributes, along with a continuous release, to their widespread distribution. However, the fact that most frequently found CECs are highly consumed or have many possible applications cannot be neglected as a factor contributing to a widespread occurrence.

Hydrophilic contaminants are in general more present in the lower part of the basin as they are potentially leaded by water flows and by stream-groundwater interactions strongly influenced by hydraulic infrastructure. Thus, potential actions should also focus on the dam system. For water supply in urban areas, usage of water from the dam S19 should be prioritized. The sample collected from this dam showed a total CECs concentration of 687 ng/L, whereas dams S20 and S21 presented a total CECs concentration of 3076 and 3616 ng/L, respectively. Even though dam S19 presents Cl^{-}-Na^{+} facies (Fig. S1) and 5040 µS/
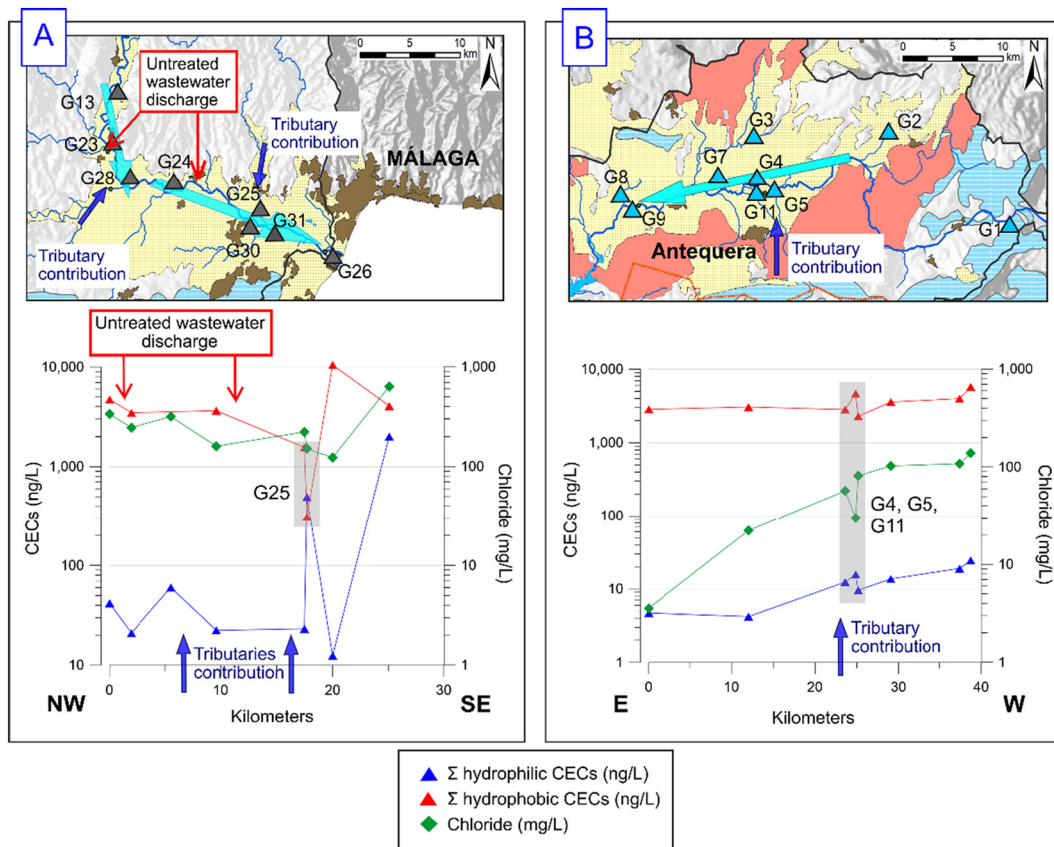
Fig. 9. Hydrophilic CEC, hydrophobic CEC and chloride groundwater content variation from northwest to southeast in sector A (A) and from east to west in sector B (B) in line with main groundwater flows direction. Note: Blue arrows broadly represent groundwater flow pathways. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

cm (Table S2), salinity is an easier problem to solve. All water led to the water supply system in the lower basin is anyhow previously treated with inverse osmosis in a brackish water desalination plant. Nevertheless, the only solution for diminishing CECs content in water coming from the dams and used for irrigation would involve a control or water treatment at sources.

Hydrochemistry and previous studies about water quality in the Guadalhorce River basin especially revealed the significance of agricultural practices and intensive livestock production activities as contaminant sources (Urresti-Estala et al., 2015). Organic pollution analysis evinces the impact of activities related to urban centers (domestic actions) and industries. This is mainly reflected by fragrances concentrations in surface water samples close to urban areas with and without Wastewater treatment plants. Although nowadays wastewater treatment is not fully effective for CECs removal (Gogoi et al., 2018), obtained results point out the lack of WWTP as a serious problem yet to be solved in the studied region since the load of some pollutants detected at the highest concentrations could be diminished by regular wastewater treatments (Carballa et al., 2004, 2005). Control improvement and evaluation of potential hazards regarding CECs release through application of biosolids as fertilizer in this area are also suggested since this is a potential source of the most frequently found contaminants in the area.

A snapshot of the situation of the basin regarding water pollution by organic chemicals has been provided and further research will rely on obtained results. These showed a ubiquitous presence of organic pollutants in the Guadalhorce River basin as they were detected in all samples suggesting the need to carry out more complete monitoring campaigns in the future including rain water sampling. Soil monitoring is also recommended as it can be a reservoir of hydrophobic non-ionic compounds (Clarke and Smith, 2011) such as synthetic musks (Chase

et al., 2012; Biel-Maeso et al., 2019). Additionally, long-time monitoring would be necessary to better evaluate organic chemicals response or correlations to different hydrological and hydrochemical parameters. The monitoring campaign conducted for this work was performed on March, at the end of the wet season. Pollutants occurrence might change in summer because of different hydrological circumstances, a general growth of tourism in the area or an increase of solar irradiation promoting photodegradation for some pollutants.

CRediT authorship contribution statement

M.I. Llamas-Dios: Writing – original draft, Investigation, Writing – review & editing, Visualization, Formal analysis. **I. Vadillo:** Conceptualization, Methodology, Formal analysis, Funding acquisition, Project administration, Supervision, Data curation. **P. Jiménez-Gavilán:** Conceptualization, Methodology, Formal analysis, Supervision, Data curation. **L. Candela:** Conceptualization, Formal analysis, Supervision. **C. Corada-Fernández:** Methodology, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.147822.

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