Research papers

Hydrogeological, hydrodynamic and anthropogenic factors affecting the spread of pharmaceuticals and pesticides in water resources of the Granada plain (Spain)

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ABSTRACT

The anthropogenic organic contaminants contemplated in the environmental legislation, as well as those of emerging concern, threaten the quality of water resources to a degree that remains largely unknown. Contaminant exposure in the aquatic environment is a crucial element if a full understanding of the risk is pursued. There are still many uncertainties about the occurrence of organic pollutants and behavior in the hydro(geo)logical media in large scale areas. The case study of the unconfined aquifer of the Granada Plain (approximately 200 km^2) is presented here. Two surface and groundwater monitoring campaigns were conducted (March 2017 and June 2018). In total, 41 out of 171 target organic pollutants were detected, at least once: 17 pharmaceuticals or drugs of abuse, 21 pesticides or their metabolites and three polyaromatic hydrocarbons. In addition, physico-chemical parameters were measured during the monitoring campaigns and hydrochemical parameters and stable isotopes (δ^2H, δ^{18}O, δ^{13}C) were analyzed. Statistical tests confirmed the significance of seasonal changes for some of these parameters (e.g., EC, Cl$^-$, F$^-$, δ^{18}O, δ^{13}C), revealing the influence from snowmelt water input on streams and the intensification of irrigation. In March 2017, the group of pesticides (largely represented by triazines) predominated, whereas the frequency of detection of pharmaceuticals increased substantially in June 2018. Results suggest four main factors affecting the spatial and seasonal variation of organic pollutants in the aquifer: the anthropogenic factor determining the period of contaminant release throughout the year (pesticide application period and growth of tourism) along with irrigation practices that include reclaimed wastewater; unsaturated zone thickness; hydraulic gradient and river-groundwater hydraulic connection. The latter can be especially important in the case of those contaminants whose main path of entry into the aquatic environment occurs through wastewater discharge into streams (i.e., pharmaceuticals).

1. Introduction

A contaminant of emerging concern (CEC) is known as such not only because it has been recently considered to cause known or suspected adverse ecological or human health effects (Stuart et al., 2012) but also because they remain largely unregulated in the field of water policy (Daughton, 2004). Nonetheless, the importance of learning more about their occurrence, harmful potential and environmental behavior, has also been recognized and highlighted by institutions and the scientific community. According to Directive 2013/39/EU (European Parliament and of the Council, 2013), the European Commission must establish a Watch List that includes substances that can be of concern and for which information must be gathered. To date, three Watch Lists have been set out (European Commission, 2020) which include substances that are essentially pharmaceuticals and pesticides. Similarly, a Watch List for pollutants in groundwater, including emerging contaminants, has also

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been demanded (European Commission, 2014; Lapworth et al., 2019).

Although pesticides are pollutants contemplated in the environmental legislation (European Parliament and Council of the European Union, 2008) and the use of some of said pollutants, such as atrazine, has been banned (European Commission, 2004) due to its endocrine disruption potential (Hayes et al., 2011) and other harmful effects, they continue to be detected in the aquatic environment at concentrations still above their limit (Silva et al., 2012; Sassine et al., 2016). Moreover, relatively few groundwater studies targeting contaminant metabolites, such as those resulting from pesticide degradation, have been undertaken; these by-products can also be of concern (Bunting et al., 2020).

The potential adverse effects of emerging pollutants to human health or to ecosystems have also been researched and reviewed (López-Pacheco et al., 2019; Lei et al., 2015; Pereira et al., 2015). However, in order to fully understand the risk that CECs may entail, the exposure must be defined, and this is why hydrogeological studies are essential (Mas-Pla, 2018). Large-scale studies are very valuable to understand the spatial occurrence and trends of CECs, and will help build a foundation for future regulation. Yet these studies are not as frequently conducted as they should (Bunting et al., 2020). Furthermore, the spatial distribution of anthropogenic organic contaminants is challenging to assess, as it can be affected by several factors such as the spatial and temporal distribution of pollution sources. Since wastewater treatment is not fully successful at eliminating CECs (Carballa et al., 2004; Carballa et al., 2005), wastewater discharge into streams acts as the main path of entry into the aquatic environment, which is the reason why emerging contaminant research has mainly focused on surface water (Stuart et al., 2012). Other factors need to be considered: the influence of the hydraulic context on CECs occurrence was observed by Corada-Fernández et al. (2017) who compared periods of droughts and extreme rainfall events; Lutri et al. (2020) determined the relationship between the presence of glyphosate and its main metabolite and shallowest water table and low flow velocity. The physico-chemical properties of the pollutants themselves can grant them different environmental behaviors (Massmann et al., 2006; Schaffer and Licha, 2015; Martínez-Hernández et al., 2016). Llamas-Dios et al. (2020) pointed out the potential role of hydraulic infrastructure on spatial distribution of hydrophilic CECs (i.e. pharmaceuticals).

In this study we present the spatial distribution and seasonal variation of CECs and other regulated organic pollutants in water resources of the *Vega de Granada* aquifer (hereafter VG aquifer; *Vega* means irrigated plain in Spanish), an alluvial aquifer of 200 km^2, approximately. One-hundred and seventy-one organic pollutants were analyzed including pharmaceuticals, pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and brominated diphenyl ethers (BDEs). Data interpretation focused on the distribution of pharmaceuticals, pesticides and their metabolites, according to their higher frequency of detection, as it will be seen in following sections. Two monitoring campaigns were carried out in order to assess the importance of aquifer recharge processes associated with seasonal changes (natural and anthropogenic).

The VG aquifer is an alluvial aquifer covered by agricultural lands and urban areas demanding an increasing volume of water resources, from surface streams and the subsoil. Human activities have led to a general increase of salinity (Castillo et al., 2010) and high nitrate contents in groundwater due to decades of fertilizer use (Castillo, 2005; Rodriguez-Galiano et al., 2018) and to a decrease of water recharge and renewal rates (Castillo et al., 2010). Microbiological contamination has also proven to be a sanitary problem in this region (Castillo and Ramos-Cormenzana, 2002).

Luque Espinar et al. (2015) conducted a study on the distribution and seasonal variation of six CECs in water resources of Granada city metropolitan areas, observing water pollution by pharmaceutical active compounds (ibuprofen, paracetamol, caffeine and pantoprazole) and even affection on the crops, which are usually irrigated with wastewater. Luque-Espinar and Chica-Olmo (2020) observed an important affection

by wastewater in the entire aquifer; amoxicillin, caffeine, paracetamol and ibuprofen were detected in collected vegetables. As mentioned, in the present study the number of target pollutants to be analyzed in water resources has been expanded.

The purpose of this study is to investigate the occurrence and distribution of pharmaceuticals and other regulated organic pollutants (i.e., pesticides) in surface and groundwater of the highly impacted VG aquifer and to assess seasonal differences. To do so, the following specific objectives are pursued: 1) to provide a description of the system regarding water pollution by organic chemicals; and 2) to define the context of the groundwater system during both campaigns using hydrochemical data and environmental isotopes. The aim is to distinguish the importance of the role played by the different possible factors (i.e., hydrogeological characteristics of the aquifer, hydrodynamic context, physico-chemical properties of the pollutants, human practices) on the spread of organic pollutants in the VG aquifer.

2. Study area

The Vega de Granada (VG) plain extends over 200 km^2 and is located in the south of the Iberian Peninsula, in Spain (Fig. 1). The VG Plain is at the center of the Upper Genil River catchment (2,950 km^2), also known as the Granada basin. It is the largest water consumption zone within the catchment area, meeting the demands of 120 km^2 of irrigation lands and 550,000 inhabitants, approximately (Castillo et al., 2010). The Genil River starts in the Sierra Nevada Mountain Range on the east and flows through the plain in a westerly direction, where it is joined by several tributaries. The elevation of the plain is about 550 m a.s.l., the Sierra Nevada Mountains reaching 3,470 m a.s.l. The average temperature in the plain is around 15–16 °C whereas that of the Sierra Nevada ranges from 5 to 6 °C at an elevation of 2,550 m a.s.l. Mean annual precipitation is 490 mm/year in the plain and about 1,000 mm/year in the upper mountains (Kohfahl et al., 2008).

The Granada basin (Fig. 1) consists of an outcrop of Neogene to Quaternary sediments overlying the NE-SW trending contact between the External and Internal Zones of the Betic Cordillera. The sequence of the sedimentary materials is over 2 km thick in some areas. Uplift of the cordilleras that started in the late Miocene generated normal faults that defined the basin limits and caused the deposition of alluvial and delta fans along the edges. The aquifer corresponds to the Holocene (Quaternary) detritic sediments filling the tectonic depression, which presents a sedimentary multilayered structure with levels of gravels, sand, silt and clay, as a result of the coalescence between river sedimentation and that of the alluvial fans. Aquifer thickness reaches up to 250 m in the center part (Mateos et al., 2017). Low permeability Neogene and Quaternary materials showing variable lithology bound the VG aquifer, except for a Jurassic carbonate outcrop located in the north (DPG-IGME, 1990). The latter consists of limestones and dolostones overlying a Triassic evaporitic basement. Miocene (Neogene) materials form the basement of the alluvial sediments of the aquifer (DPG-IGME, 1990). The general Neogene sedimentary sequence is composed of calcarenites, terrigenous sediments and evaporites (Kohfahl et al., 2008; Fig. 2). The Holocene VG aquifer boundaries are closed, except for those in contact with the Jurassic carbonates and those in contact with coarse-grained upper Pliocene-lower Pleistocene materials at the eastern boundary and with Quaternary alluvial fan materials in the southeast. The VG aquifer fine-grained substratum is impervious due to its content in clays and silts (Luque-Espinar et al., 2002).

Transmissivity of the VG aquifer ranges between 100 and 40,000 m^2/day, with an average of 4,000 m^2/day (Castillo et al., 2010). Along the central axis of the aquifer and in the southeastern part, in zones close to the Genil River and the Monachil and Dílar Rivers, the aquifer consists mainly of fluvial gravels and sands. Thus, the highest transmissivity values are observed in these zones. Coarse sediments with thicknesses of up to 150 m have been recorded at the central zone of the aquifer. Clay content increases towards the boundaries and a minimum clay content
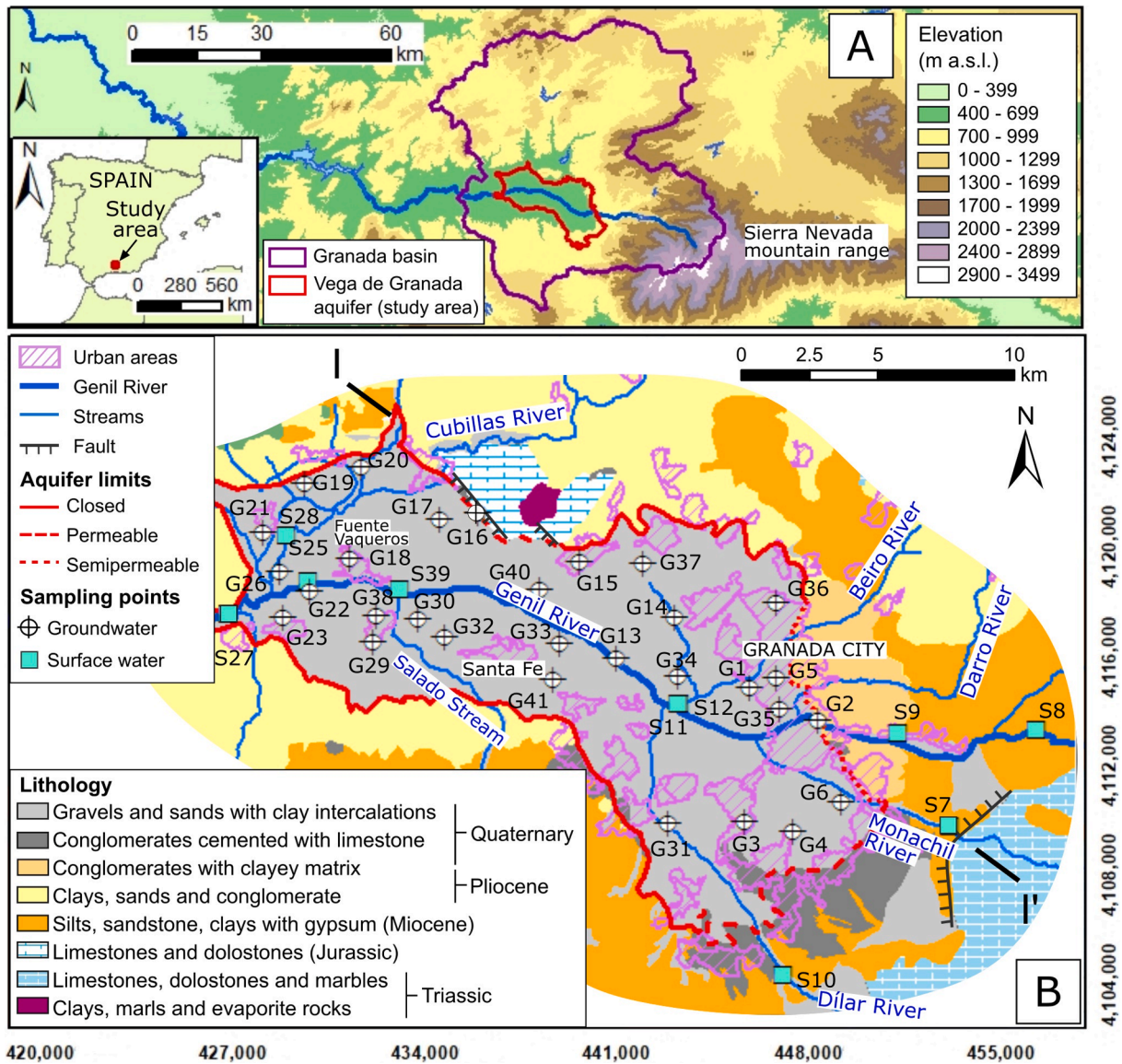
Fig. 1. Location, topographic map (A; IAECA, 2019) and lithological map (modified from Castillo-Martín, 1986; IGME, 1990) of the study area with sampling points (B).

of 80% has been estimated in the northeastern part of the aquifer (Mateos et al., 2017) where the steepest hydraulic gradient is observed (Fig. 3).

Average renewable water resources of the VG aquifer are estimated to be 160 hm^3/year (Castillo et al., 2010). Aquifer water recharge comes mainly from surface runoff generated in the Granada basin. Nevertheless, the main recharge area is located in the southeastern sector, where most tributaries join the main riverbed (Chica-Olmo et al., 2014). Thus, water recharge from surface water infiltration takes place essentially thanks to infiltration from the Genil, Dílar and Monachil Rivers (CHG, 2021; Fig. 1). Infiltration of surface runoff is strongly driven by irrigation through a dense network of irrigation channels and ditches that takes up part of this surface water. This water input is estimated to be 126 hm^3/year. Rain infiltration over the permeable surface of the aquifer adds 24 hm^3/year, and contribution from adjacent aquifers is around 10 hm^3/year (Castillo et al., 2010), which is likely to occur mainly at the southeastern boundary of the aquifer, near to the more permeable carbonate rocks (Kohfahl et al., 2008). Aquifer discharge occurs, on the one hand, through natural discharge in the western sector of the aquifer, downstream from the town of Fuente Vaqueros, through springs and diffuse sources towards the Genil and Cubillas Rivers (IGME, 1990). The average value of this output has been estimated at 110 hm^3/year. On the other hand, net groundwater abstraction through wells accounts for the remaining 50 hm^3/year, 85% for agricultural use and 15% for urban water supply (Castillo et al., 2010).

As mentioned, stream-aquifer hydraulic connection is different in the eastern and western parts. In the eastern sector, a river disconnected from the water table loses water towards the aquifer, whereas the river gains water from the aquifer predominantly near the western boundary (IGME, 2009). In the eastern part, below the city of Granada, the unsaturated zone of the aquifer reaches its maximum thickness, with minimum thicknesses found in the western part (Fig. 3).

There are two wastewater treatment plants (WWTP) treating wastewater from the Granada area (Fig. S1). In these facilities, 42 hm^3 and 37 hm^3 of wastewater was treated in 2017 and in 2018, respectively. Purification processes consist of preliminary treatment, a primary sedimentation process, secondary biological treatment and secondary sedimentation. Treated and untreated urban wastewaters are directly released into ditches of the irrigation network or into riverbeds, from which water is also used for irrigation (Robles-Arenas et al., 2012). The
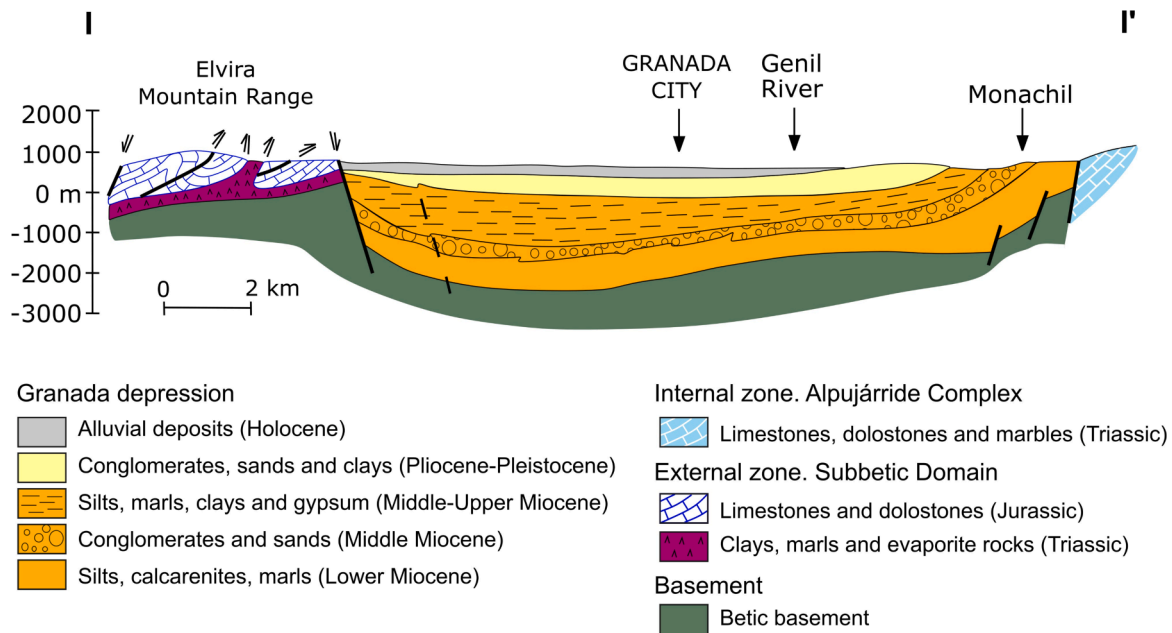
Fig. 2. Geological cross-section modified from IGME (2009). I-I' location indicated in Fig. 1.
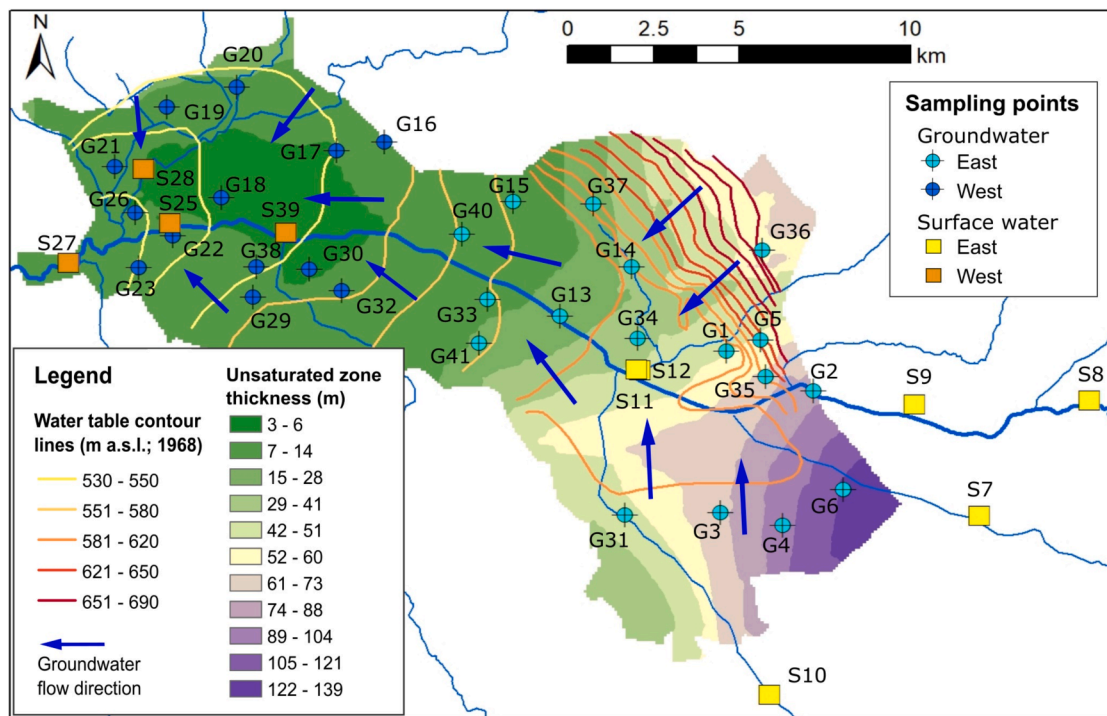

Fig. 3. Unsaturated zone thickness (modified from Rodriguez-Galiano et al., 2018) and water table contour lines (modified from Trac, 1968; Mateos et al., 2017) of the VG aquifer and location of surface water (SW) and groundwater (GW) sampling points for this study.

location and magnitude of urban wastewater discharge permitted by the basin authority can be seen in Fig. 4.

3. Materials and methods

3.1. Water sampling and measurement of physico-chemical parameters

Two monitoring campaigns were conducted, one in March 2017 and in June 2018. They consisted of the collection of 30 groundwater samples and 10 surface water samples (Fig. 1). Groundwater samples were collected mainly from irrigation wells from the alluvial unconfined aquifer (VG aquifer). Continuous pumping was performed before collecting the sample. Surface water samples were collected from the Genil River and smaller tributaries. Sampling points are classified in two groups: those situated in the eastern part of the plain and those situated in the western part, based on the aforementioned differences between the two aquifer sectors (Fig. 3).

Water samples were filtered using a 0.45 μm Millipore® filter (Merck KGaA. Darmstadt, Germany). Sterile high-density polyethylene bottles (120 mL) sealed with inverted cone caps were used to store water
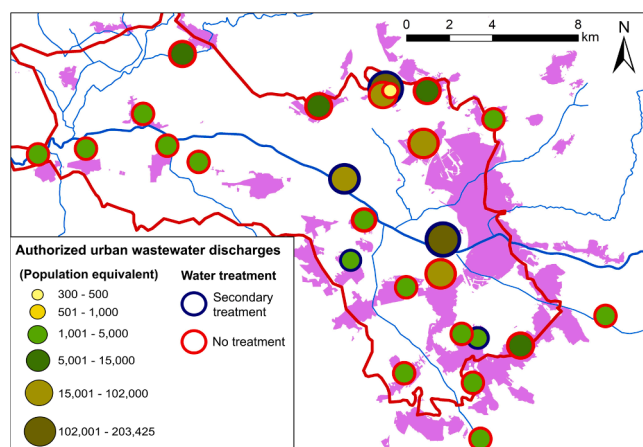
Fig. 4. Urban wastewater discharge into the environment approved by the basin authority (CHG, 2013).

samples for hydrochemical and isotopic analyses. Water samples used for organic contaminants analysis were stored in sterile amber glass bottles (1L) with Teflon caps. Bottles were rinsed before sampling, carried in an ice-filled cool-box and stored in a fridge ($< 4\ ^\circ$C) until analysis. Physico-chemical parameters (pH, temperature, electrical conductivity, redox potential and dissolved oxygen) were measured with a portable multi-parameter probe (Hach-Lange HQ40d; Hach, Loveland, CO, USA).

3.2. Water major and minor ions and isotopic analysis

Major and minor water ions were determined by ion chromatography using a Metrohm 881 Compact IC Pro (HPLC). Water stable isotopes δ^2H and δ^{18}O (‰; Vienna Standard Mean Oceanic Water), were determined in a Picarro Water Isotope Analyzer L2120i (laser spectroscopy). δ^{13}C from dissolved inorganic carbon (‰; Vienna Pee Dee Belenmite) was determined in a Picarro Carbon Isotope Analyzer G1111i-CRDS. Hydrochemical and isotope analyses were conducted at the laboratory of the Centre for Hydrogeology of the University of Malaga. The PHREEQC code was used to calculate the state of saturation (saturation index) for calcite (Parkhurst & Appelo, 1999).

3.3. Organic contaminant analysis

Water samples were analyzed for 171 organic pollutants (Table S1). Analyses of pharmaceutically active compounds (PhACs), abuse drugs and polar pesticides and metabolites, were performed by means of on-line solid-phase extraction (SPE) followed by liquid chromatography-triple quadrupole mass spectrometry (HPLC-QqQ-MS/MS) (Shoemaker, 2015; Stoob et al., 2005). Non-polar compounds and some priority substances (PAHs, PCBs, organochlorine and organophosphorus pesticides, triazines and brominated diphenyl ethers) were analyzed by gas chromatography coupled to mass spectrometry (GC–MS), preceded by stir bar sorptive extraction (SBSE) (León et al., 2003; 2006). Organic compound analysis was conducted at the IPROMA laboratory (Castellón, Spain).

3.4. Statistical analysis

To evaluate the statistical significance of seasonal change of surface water and groundwater, the paired sample *t* test was used. The latter was applied to physico-chemical and hydrochemical parameters. The *t* test requires the differences between paired observations to be normally distributed (Helsel et al., 2020). To check the normal distribution of differences, the Shapiro-Wilk test was used. For datasets that do not follow a normal distribution, the non-parametric Wilcoxon signed-rank test was applied (Helsel et al., 2020). The analyses were performed using

the 'stats' package in R software (R Core Team, 2020). If the obtained *p*-value is below 0.05, the null hypothesis stating that the two compared groups do not differ significantly was rejected.

4. Results and discussion

4.1. Surface and groundwater hydrochemical composition

Descriptive statistics of measured physico-chemical parameters and hydrochemical results are available in the Supplementary Material section (Tables S2 and S3). A spatial variability of hydrochemical characteristics is observed in the study area regarding both surface water and groundwater (Fig. 5; Fig. 6). Calcium and magnesium bicarbonate low-mineralized type water is predominant in the eastern part, potentially as a consequence of water input coming from the Sierra Nevada Mountain Range through riverbeds. In contrast, mixed facies with a higher level of mineralization are most commonly found in the western part, indicating different factors affecting water quality other than rock-water interaction (i.e., impact of human activities). Sulphate-sodium, chloride-sodium and sulphate-calcium facies near the southern aquifer limit reflect the influence of the evaporitic materials from the Miocene deposits. The electrical conductivity (EC) mean value was higher in the western sector in both campaigns: a mean value of $1,453 \pm 538$ µS/cm was recorded in groundwater in the western sector in March 2017 ($1,767 \pm 567$ µS/cm in June 2018), whereas a mean value of 824 ± 266 µS/cm was recorded in groundwater from the eastern sector in March 2017 (977 ± 255 µS/cm in June 2018). As regards surface water, a mean value of $1,162 \pm 166$ µS/cm was recorded in the western sector in March 2017 (909 ± 490 µS/cm in June 2018) and a mean value of 333 ± 69 µS/cm was recorded in the eastern sector in March 2017 (176 ± 51 µS/cm in June 2018). Hence, in terms of temporary variation, groundwater EC values were significantly higher ($p < 0.05$; see Table S4) in June than in March. However, fluoride is the only ion increasing its concentration significantly in groundwater in June. In contrast, surface water EC values were significantly lower in June than in March. This EC decrease was statistically significant only in the eastern sector probably because the streams are influenced in the west by groundwater quality. Ca^{2+}, Mg^{2+}, Na^+, HCO_3^-, SO_4^{2-}, and Cl^- diminish significantly ($p < 0.05$) in surface water in the eastern sector, which is consistent with the EC decrease. However, surface and groundwater types remain very similar in both monitoring campaigns, as observed in Piper diagrams (Fig. 5).

Nitrate concentration values in groundwater surpass the threshold value (50 mg/L; European Parliament and the Council of the European Union, 2006) in both sectors, although a higher mean value is determined in the western sector, indicating worse water quality. Nitrate concentrations have been high for decades in the VG aquifer as a result of a fertilizer input for crops and low renewal rates (Castillo et al., 2010; Plata-Bedmar and Greciano-González, 2018). No seasonal change in nitrate concentration has been statistically significant (p greater than 0.05).

4.2. Surface and groundwater stable isotopes

Groundwater from the eastern sector is more depleted in oxygen-18 (mean $= -8.4‰ \pm 0.5$ in both monitoring campaigns) and deuterium (mean $= -55.5‰ \pm 2.9$ in March 2017 and $-56.0‰ \pm 3.5$ in June 2018) than groundwater in the western sector (δ^{18}O mean value $= -7.4‰ \pm 1.0$ in March 2017 and $-6.6‰ \pm 2.3$ in June 2017; δ^2H mean value = -51.3 ‰ ± 5.3 in March 2017 and $-55.2‰ \pm 7.5$ in June 2018; Fig. 7). δ^{18}O spatial variation can be observed in Fig. 8 for both monitoring campaigns. Similar isotopic signals of groundwater in the eastern sector and surface water coming from the east reveal the significance of these streams as a source of groundwater. Little recharge contribution from rainwater is estimated, since its δ^{18}O signal is -7.5 ‰ (Delgado-Huertas et al., 1991).

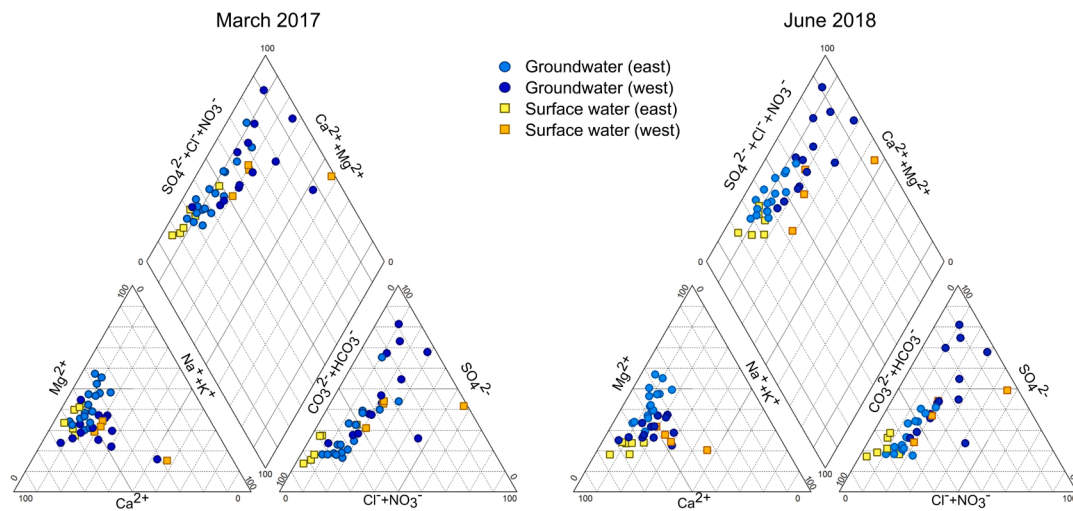Although mean values do not change substantially in groundwater

Fig. 5. Piper diagram showing hydrochemical facies for the two monitoring campaigns.
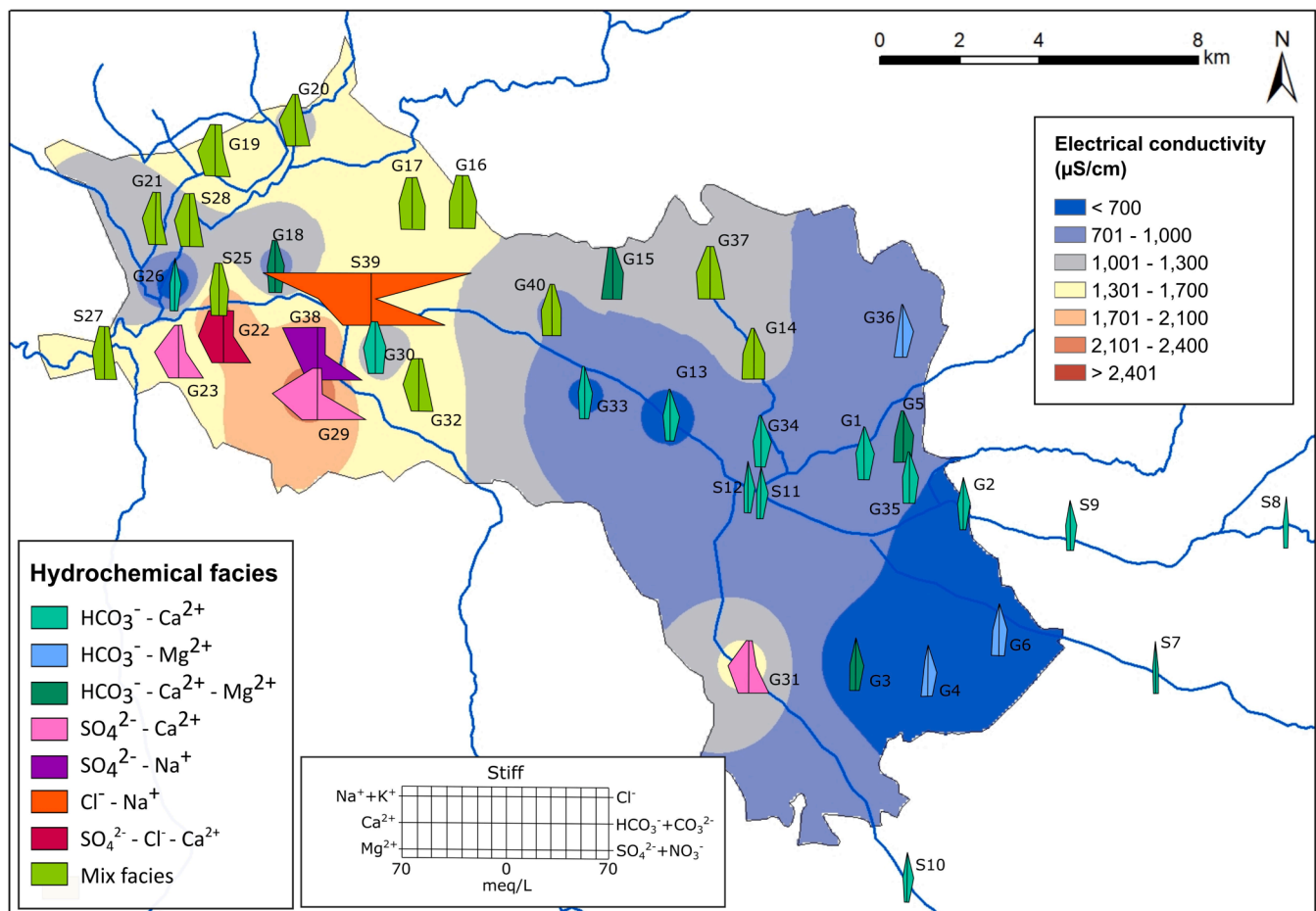

Fig. 6. Electrical conductivity contour lines and water types (Stiff diagrams). Name of surface water and groundwater samples use S and G as prefix, respectively. Only data obtained from March 2017 monitoring campaign is represented in this figure since water types do not change substantially between the two monitoring campaigns (Fig. 5).

between the two monitoring campaigns, some difference can be observed. In the June 2018 campaign, few more extreme values were recorded. More depleted δ^{18}O values were recorded near the southeastern boundary of the aquifer and slightly more enriched δ^{18}O values were observed in the western part (Fig. 8). This isotope enrichment suggests an intensification of irrigation during this warmer season.

Evaporation from irrigation return flows can cause enrichment in oxygen-18 in groundwater (Urresti-Estala et al., 2016). On the other hand, surface water in the east was significantly more depleted in this isotope (Fig. 7, Fig. 8) in June 2018 (mean = −9.4‰ ± 0.5) than in March 2017 (mean = −8.5‰ ± 0.7). During spring and summer, these rivers receive meltwater from the Sierra Nevada (Fig. 1) with lighter
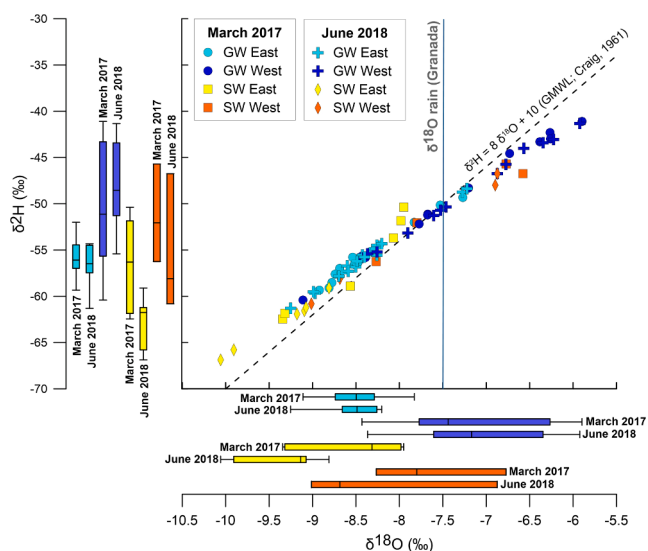
Fig. 7. Water stable isotopes (δ^{18}O and δ^2H in ‰) of monitored surface water and groundwater of the VG aquifer in both monitoring campaigns and average δ^{18}O of rain water in Granada (Delgado-Huertas et al., 1991).
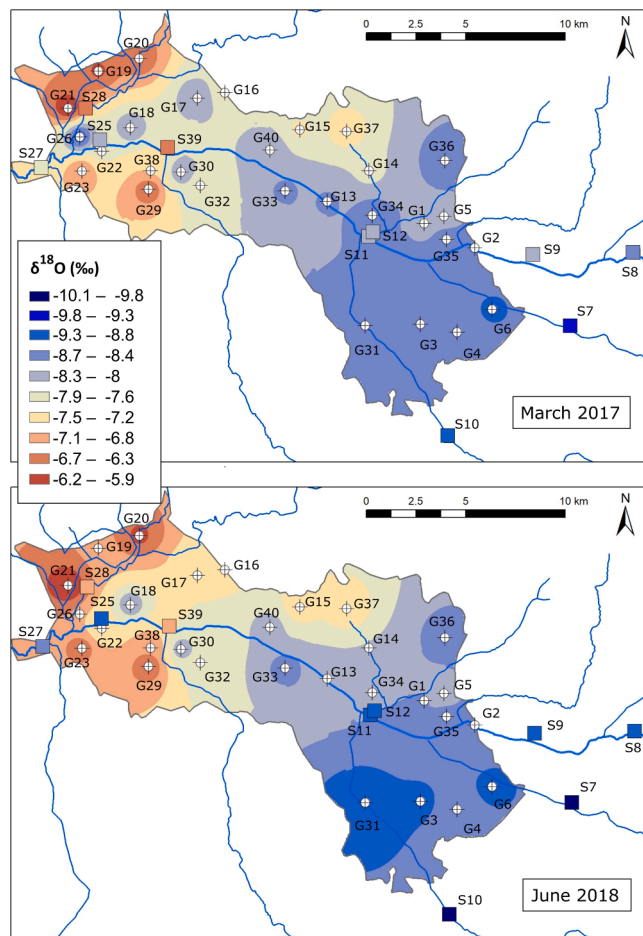

Fig. 8. δ^{18}O (‰) groundwater contour lines and δ^{18}O (‰) of surface water sampling points (squares).

δ^{18}O because of the high-altitude precipitation. River-aquifer interactions in the east can cause oxygen-18 depletion in groundwater near the southeastern sector where the rivers lose water towards the

aquifer. Additionally, the statistical analysis showed that the seasonal δ^{18}O variation was only significant in the case of surface water in the eastern sector ($p < 0.05$).

Surface water from rivers flowing from the east was also more enriched in carbon-13 in June than in March (Fig. 9). An increase in δ^{13}C can indicate CO_2 removal from water by photosynthesis, which is more intense in warmer months (Atekwana & Krishnamurthy, 1998). Surface water temperature in this sector was also significantly greater ($p < 0.05$) in June (mean = 13.4 °C ± 0.9) than in March (mean = 10.9 °C ± 1.5). The potential photosynthesis increase along with dilution due to melt-water contribution can be the cause of a lower bicarbonate concentration in these surface water sampling points in June (Table S3).

The isotopic composition (δ^{13}C) of surface water in the western sector is not very similar to that of the eastern sector since this stretch of the river receives water from the aquifer. Thus, groundwater influences the isotopic signal of surface water in this case.

A significant decrease in δ^{13}C in groundwater ($p < 0.05$) suggests water infiltration from the unsaturated zone. When waters infiltrate to the subsurface, they equilibrate with soil CO_2. In most temperate landscapes, soil CO_2 is generally about –23 ‰ (Clark & Fritz, 1997).

4.3. Occurrence and spatial and seasonal variation of target organic pollutants according to usage group

Organic compound analysis (Table S1) showed that, in the March 2017 monitoring campaign, 29 out of 171 analyzed compounds were found in at least one sample: 11 PhACs, 16 pesticides and two PAHs. In the June 2018 campaign, 33 compounds were detected: 15 PhACs, 14 pesticides, and two PAHs. Hence, four more pharmaceuticals and two less pesticides were found in the second campaign. The frequency of detection and average concentration of all detected organic contaminants in surface water and in groundwater is shown in Fig. 10 and Fig. 11, respectively.

In both monitoring campaigns, most PhACs were detected more often in surface water than in groundwater (10 out of 11 in March 2017 and 12 out of 15 in June 2018). This can be a consequence of the importance of wastewater discharge into streams as a path of entry of these pollutants into the aquatic environment, as well as of aquifer attenuation capacity.

As regards pesticides, 7 out of 16 were detected more often in groundwater in March 2017; in June 2018, only 3 out of 14 were detected more frequently in groundwater. These are all triazines, which
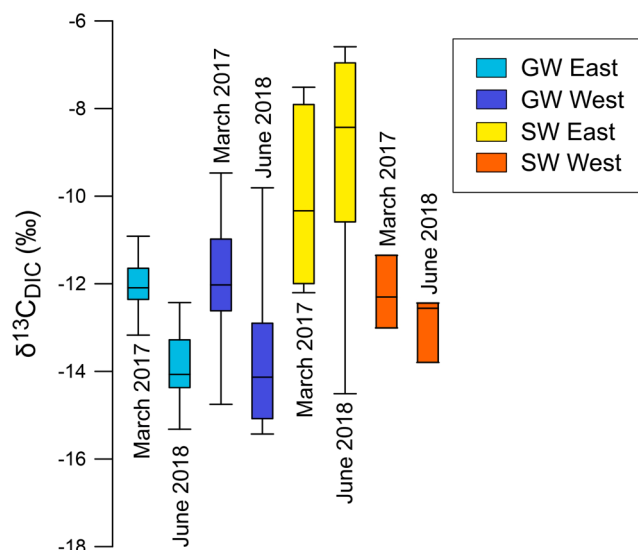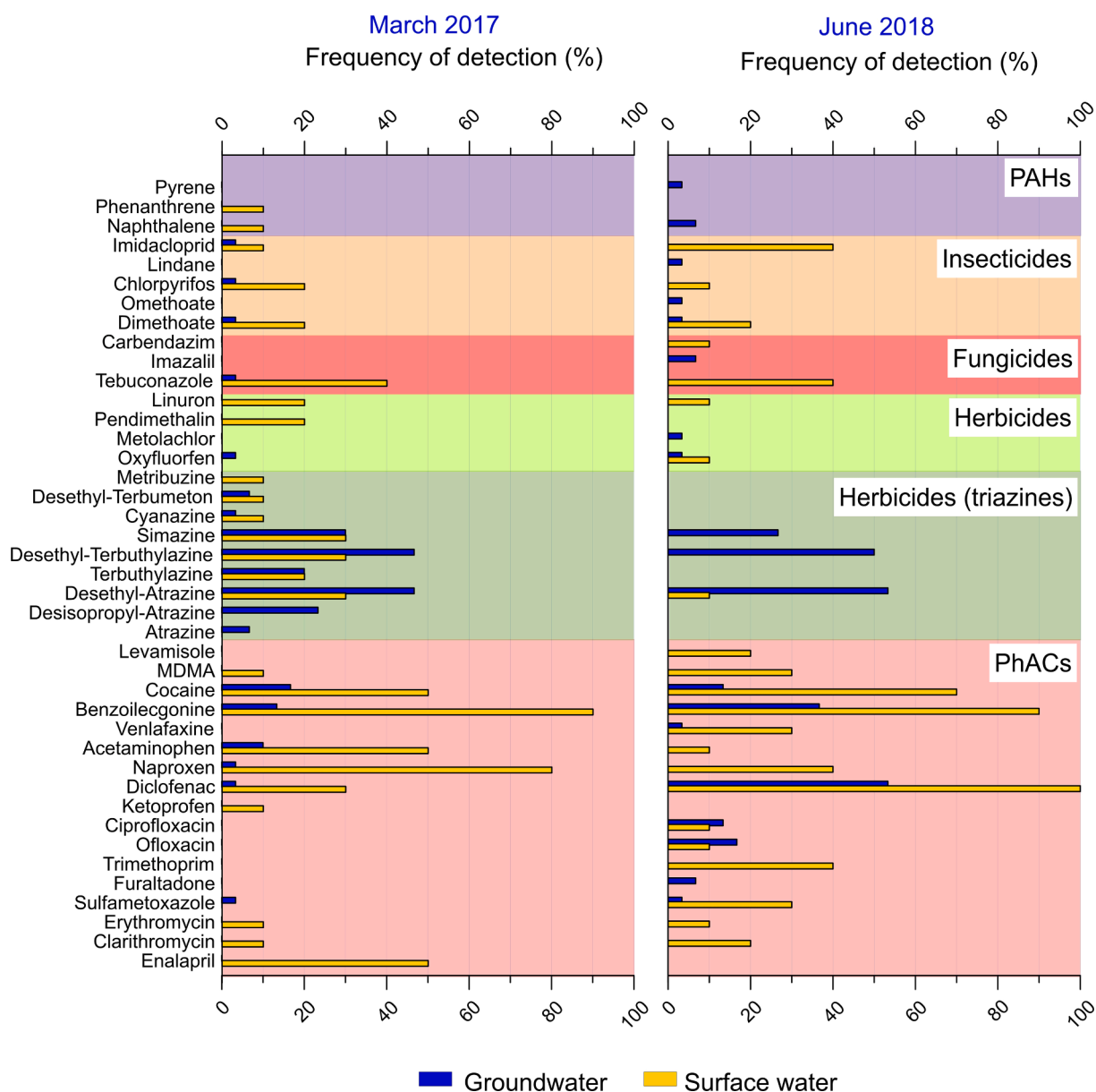

Fig. 9. δ^{13}C$_{DIC}$ (‰) of monitored surface water and groundwater in the two monitoring campaigns.
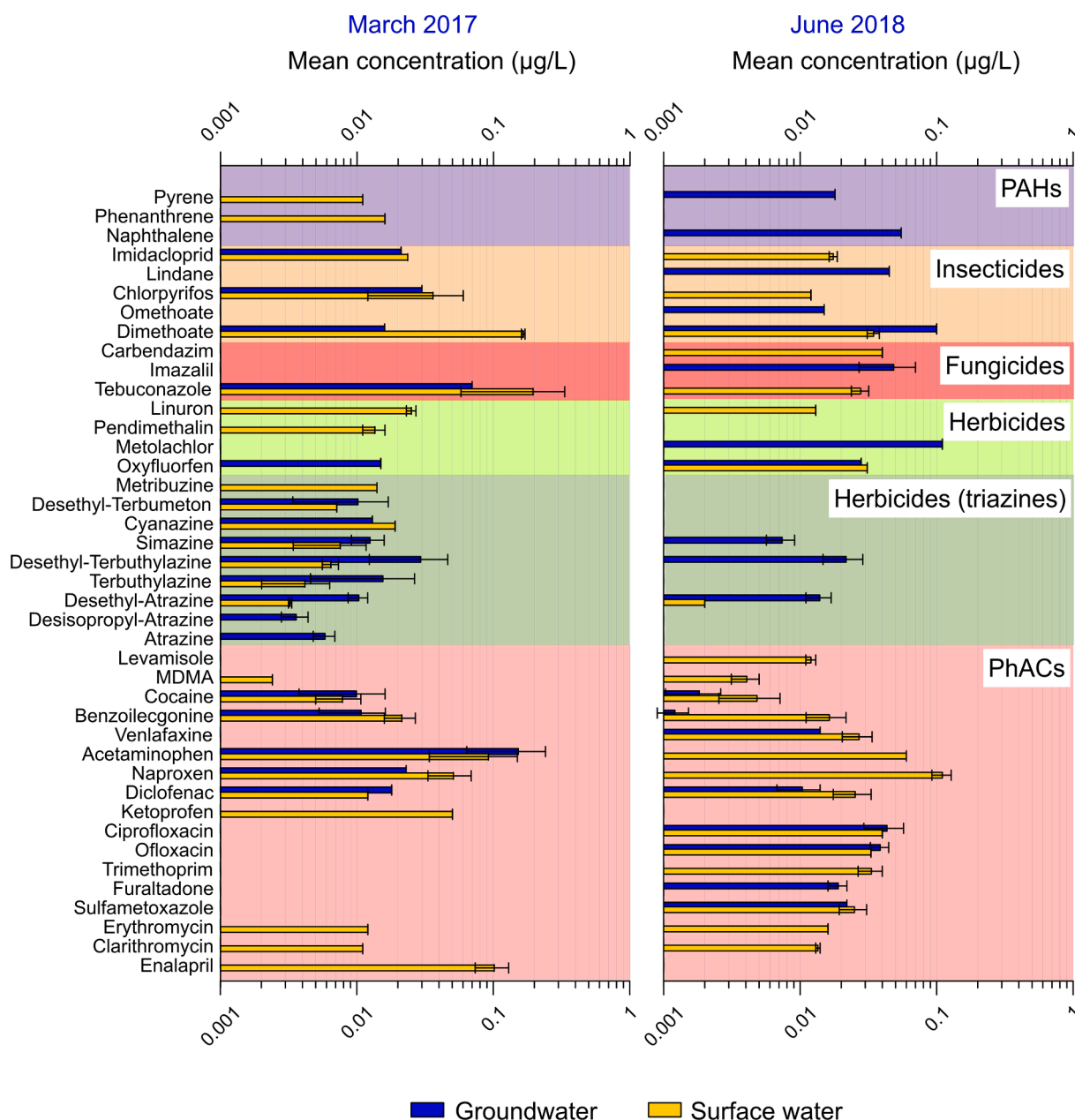
Fig. 10. Frequency of detection (%) of organic contaminants in surface water and groundwater from the VG aquifer in the two monitoring campaigns (March 2017 and June 2018). Legend: PAHs: polycyclic aromatic hydrocarbons; PhACs: pharmaceutical active compounds.

are herbicides. The rest include other herbicides, fungicides and insecticides. Herbicides are applied directly to the soil in agricultural lands as a diffuse source and they would be expected to reach the water table through wash-off and release from the soil granulates before reaching the streams. In contrast, fungicides and insecticides are generally applied to the foliage and thus, they are more susceptible to reach the streams through spray-drift. Variation differences between the two seasons might be due to the use of the compounds (target pest) and thus, the time of the year in which these are applied. Thirteen out of the total number of pesticides detected in both campaigns (21) are herbicides: all of the triazines, oxyfluorfen, metolachlor, pendimethalin and linuron. The frequency of detection of 11 of them, including all triazines, decreases in June, whereas the frequency of detection of the rest remains largely similar or increases. Among triazines, only simazine, desethyl-terbuthylazine and desethyl-atrazine remain at detectable concentrations in the second campaign, and they do almost exclusively in groundwater. This can mean that they are no longer being applied to the fields; thus, excess of these pesticides would not run off and reach the streams, but the remaining molecules trapped in the soil and geological

media could slowly reach the water table thanks to washing by rain events or irrigation.

Regarding all data, concentrations ranged from 0.0002 μg/L for cocaine in surface water (June 2018) to a maximum of 0.6 μg/L of pesticide terbuconazole in surface water (March 2017). Minimum, maximum and mean values of organic contaminant concentrations are available in Tables S6 and S7. Priority substances naphthalene, atrazine, chlorpyrifos and simazine were detected under the Environmental Quality Standards established for these substances in surface waters (European Parliament and the Council of the European Union, 2013). Although lindane (γ isomer of hexachlorocyclohexane) was only detected in groundwater, its concentration exceeded the limit set for surface waters in Directive 2013/39/UE (greater than0.04 μg/L). In the monitoring campaign carried out in March 2017, the limit set for individual pesticides in groundwater (Directive 2006/118/EC; European Parliament and Council of the European Union, 2006) is exceeded in sampling point G23 (0.24 μg/L of desethyl-terbutilazine). In the June 2018 monitoring campaign, this limit was exceeded in sampling point G41 (0.11 μg/L of metolachlor).

Fig. 11. Average concentration (µg/L) and error bars of detected organic contaminants in surface water and groundwater from the VG aquifer in the two monitoring campaigns (March 2017 and June 2018). Legend: PAHs: polycyclic aromatic hydrocarbons; PhACs: pharmaceutical active compounds.

The following contaminants detected in this study are included in the latest Watch List (Decision (EU) 2020/1161; European Commission, 2020): pesticides imazalil and tebuconazole and pharmaceuticals ciprofloxacin, sulfamethoxazole, trimethoprim, and venlafaxine. Erythromycin and clarithromycin were the only detected pharmaceuticals that are included in the first Voluntary Groundwater Watch List, although they were found only in surface water. Therefore, none of the pollutants included in that list were detected in groundwater in this study.

Fig. 12 shows concentrations and distribution of detected organic compounds according to usage group in the study area for both monitoring campaigns. A widespread distribution and dominance of triazines is observed in March 2017, whereas pharmaceuticals gain ground in June 2018. Also, in the March 2017, 8 sampling points showed no detectable content in organic pollutants but in June 2018 this number decreases to 3 sampling points. A general increase of pharmaceuticals in June can be a consequence of a growth in tourism and an increase of water demand during summer (Murillo-Díaz et al., 2006).

A group of detected organic contaminants has been selected for discussion. The selection is based in their high frequency of detection, therefore they can provide insights into the spatial and seasonal variation. The selection includes illicit drugs cocaine and benzoylecgonine, diclofenac, desethyl-terbuthylazine, desethyl-atrazine and simazine.

4.4. Selected pharmaceutical active compounds (PhACs)

The PhACs most frequently detected (present in more than 70% of groundwater or surface water samples in any of the two monitoring campaigns) were cocaine, benzoylecgonine and diclofenac (Fig. 10).

Diclofenac was detected in one groundwater sample (0.018 µg/L) and in one surface water sample (0.012 µg/L) collected on March 2017. In the June 2018 monitoring campaign its frequency of occurrence increased substantially: it was then detected in 53% of groundwater samples (0.010 ± 0.014 µg/L) and in all surface water samples (0.025 ± 0.024 µg/L). Diclofenac is an anti-inflammatory agent and it was one of
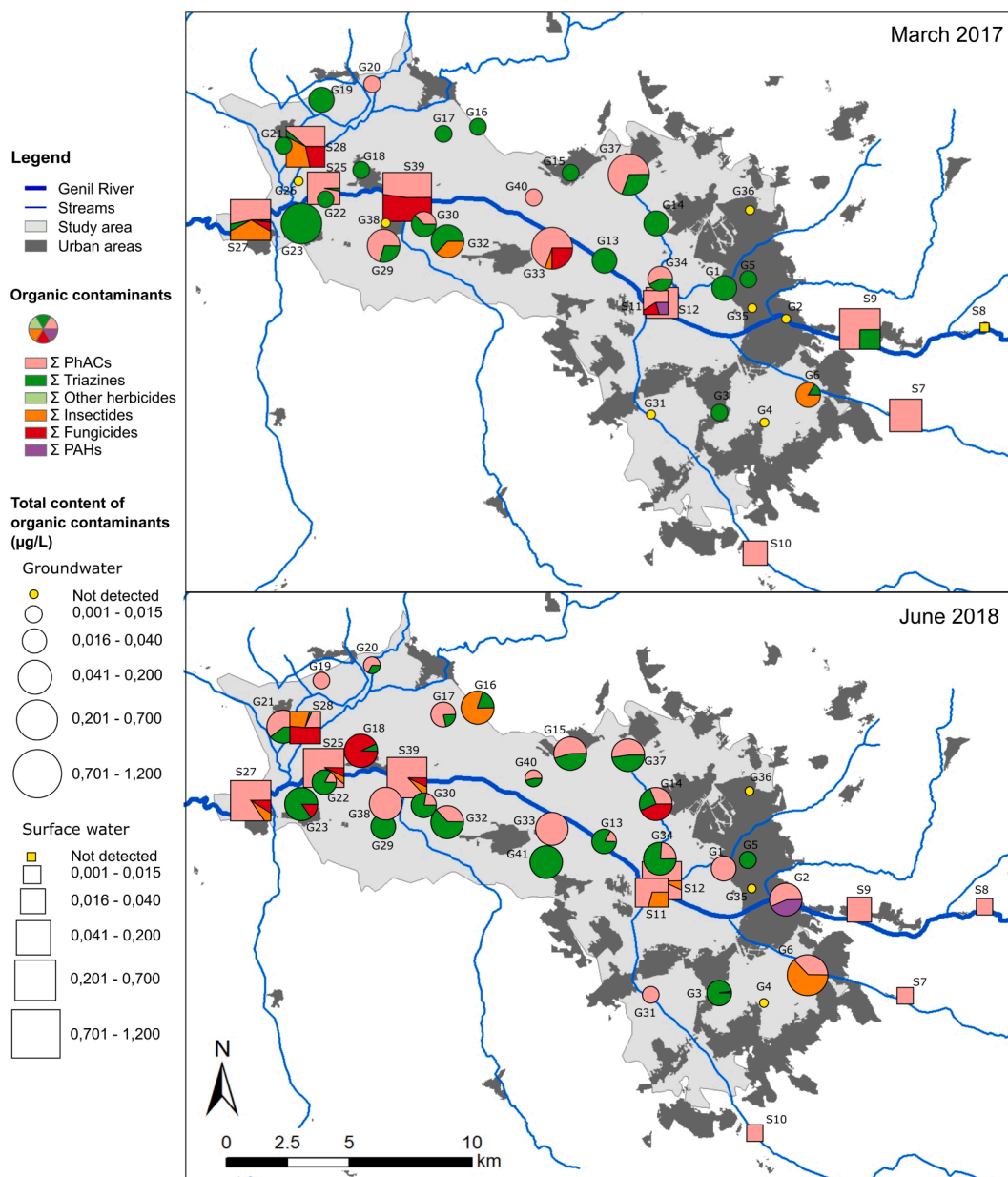
Fig. 12. Pie charts of detected organic pollutants according to usage group in groundwater (circles) and surface water (squares) for both monitoring campaigns. Total pollutant concentration is indicated by size of circles and squares.

the most reported CECs in European groundwater in recent years (Bunting et al., 2021). In spite of its relatively high octanol–water partition coefficient ($logK_{ow}$ = 4.51), diclofenac is an acidic compound with a $pK_{a,acid}$ value of 4.15, which means that only the ionized form (negatively charged) exists in solution with pH ≥ 6.15 (Biel-Maeso et al., 2017). pH field measurements ranged from 6.8 to 8.7 in this study. This characteristic facilitates the mobility of the substance in the subsurface, since it avoids sorption onto negatively charged surfaces of clays and organic matter (Schaffer and Licha, 2015). Diclofenac can be quickly removed by biodegradation in agricultural soils (<7 days), as observed by Thelusmond and co-workers (2018).

Benzoylecgonine is the major metabolite of cocaine. It is formed by hydrolysis of cocaine in the liver of cocaine users. These two substances showed a relatively high frequency of detection in both campaigns. In March 2017, benzoylecgonine was detected in 90% of surface water samples (with a mean concentration of 0.021 ± 0.016 µg/L) and in 13% of groundwater samples (mean of 0.011 ± 0.01 µg/L); cocaine was found in 50% of surface water samples (0.008 ± 0.006 µg/L) and in 16%

of groundwater samples (0.010 ± 0.013 µg/L). An increase was observed in June 2018: benzoylecgonine showed a frequency of detection of 37% in groundwater (0.001 ± 0.001 µg/L) and still a 90% in surface water (0.016 ± 0.016 µg/L); cocaine showed a frequency of detection of 70% in surface water (0.005 ± 0.006 µg/L) and 13% in groundwater (0.002 ± 0.002 µg/L).

Benzoylecgonine can remain in the body of users longer and in larger quantities than cocaine (Pal et al., 2013) and, once in the environment, cocaine can be rapidly degraded, mainly by hydrolysis, whereas benzoylecgonine can persist in the aquatic environment even after 15 days from the time of discharge (McCall et al., 2016), which can explain why it shows a more widespread distribution than its parent compound. Benzoylecgonine contains both an acidic and basic functional group, making it a zwitter ion (Skopp and Pötsch, 1999; White & Moore, 2018). Cocaine is a base with a $pk_{a,base}$ = 8.6 (Kim et al., 2019), which means that it can be present partially as a cation under environmental pH conditions. Hence, the ionized form can be more easily subjected to sorption processes, which would not be the case for the non-ionized

form. Both substances are rather hydrophilic because they have a relatively low $logK_{ow}$ (2.3 and 1.3 for cocaine and benzoylecgonine, respectively; Skopp and Pötsch, 1999), so they are expected to sorb poorly onto solid particles and be present in the aqueous phase.

4.5. Selected pesticides

Triazines were the most ubiquitous group of pesticides (Fig. 10), especially in groundwater, which is consistent with other European surveys (Loos et al., 2010; Tasca et al., 2018). Terbuthylazine is one of the most widely used herbicides, mostly because of the ban on the use of atrazine in Europe since 2004 (European Commission, 2004). However, both substances are potentially used in the area in similar amounts, since metabolites desethyl-terbuthylazine and desethyl-atrazine were the most frequently found compounds within this group, both reaching a frequency of detection of 47% in groundwater and 30% in surface water in the March 2017 monitoring campaign. In June 2018, these two compounds, along with simazine, were the only triazines detected and almost exclusively in groundwater: desethyl-terbuthylazine was found in 50% of groundwater samples; desethyl-atrazine was found in 53% of groundwater samples and in 10% of surface water samples.

Terbuthylazine is a very weak base ($pk_a = 2$), meaning that it is present as a non-ionized molecule over almost the entire pH range (Tasca et al., 2018) and its persistence in soils is attributed to a strong adsorption capacity on humic substances (Navarro et al., 2004). Its metabolite, desethyl-terbuthylazine, is more likely to pollute groundwater since it has a higher water solubility and does not bind as strongly to organic matter as terbuthylazine does (Tasca et al., 2018). Indeed, terbuthylazine has a higher $logK_{ow}$ (3.2; Tasca et al., 2018) than desethyl-terbuthylazine (1.94; Ronka and Bodylska, 2021). Similarly, atrazine and desethyl-atrazine are weak bases ($pk_a = 1.6$ and 1, respectively) and present a $logk_{ow}$ of 2.61 and 1.51, respectively. Therefore, the metabolite has a greater capacity to contaminate groundwater than the parent compound (Aelion & Mathur, 2001). The weak base simazine might behave the same way as atrazine since it has a pk_a value of 1.62 and a $logK_{ow}$ value of 2.18 (Tomlin, 1997).

Thus, the selected pesticides are less mobile in the subsurface than selected pharmaceuticals cocaine, benzoylecgonine and diclofenac, and they are also less stable in the environment: atrazine's half-life is estimated to be from 60 to more than 100 days in soil and the half-life of desethyl-atrazine was estimated, in microcosm studies, to be from just a few weeks to 100 days (Aelion & Mathur, 2001); the half-life of terbuthylazine is up to 120 days in soil and that of desethyl-terbuthylazine is up to 223 days (Tasca et al., 2018); lastly, the estimated half-life of simazine is 59 days (Candela, 2003).

4.6. Assessment of the fate of selected organic pollutants in the VG aquifer

Seasonal variation of certain measured parameters (Table S2) in groundwater and surface water reflects changing conditions in the study area. An EC decrease in surface waters in June can be a consequence of an input of low mineralized water from ice melting from the Sierra Nevada Mountain Range. More depleted oxygen-18 values were observed in groundwater samples near the eastern limit of the aquifer in the June 2018 campaign, suggesting water recharge from the streams with a lighter isotopic signal (Fig. 8). Indeed, a higher river flow rate was recorded during this season by the Guadalquivir River Basin Authority (Fig. S2). Nonetheless, an EC increase was observed in groundwater in June with respect to March, as observed in Fig. 13. This figure also shows the calcite saturation index in groundwater samples, which generally decreases in June with respect to March. This can be a consequence of water infiltration from the unsaturated zone, which was also reflected by $\delta^{13}C$ variations, as previously exposed. As water flows through the unsaturated zone, it dissolves CO_2 from the soil and has more calcite dissolution capacity and, therefore, it lowers the saturation index of this mineral. Infiltrating water might come from surface water runoff or rain but as mentioned, little contribution from rainfall is considered, especially in the eastern sector, as the $\delta^{18}O$ signal of precipitation (−7.5‰; Delgado-Huertas et al., 1991) does not fully represent that of the VG aquifer groundwater.

The EC increase in groundwater in June can be caused by irrigation, which is generally intensified in this period. Water irrigation demand is estimated at 0.4 hm³ in March and 11.7 hm³ in June in the Granada plain (Murillo-Díaz et al., 2006). Salt re-concentration and isotope fractionation potentially due to irrigation return flows are sharpened in June as shown in Fig. 14, essentially in the western sector. Fluoride concentration also increased significantly in groundwater ($p < 0.05$) in June with respect to March (Tables S3 and S4). The increase in the fluoride concentration has been considered an indicator of intensified abstraction in the VG aquifer in previous studies (Castillo & Sánchez-Díaz, 2005) because, when pumping is intensified, groundwater transfer from the Miocene and Triassic deposits is potentially enhanced, and renewal-rates diminish. Robles Arenas et al. (2012) checked the direct relationship between groundwater level rise and flood irrigation in a poplar crop near Santa Fe, where they recorded a 0.5 m rise in one day.

Water transfer from the riverbeds and from irrigation to the aquifer may generate a widespread expansion of certain organic pollutants, especially PhACs. Fig. 15 shows the relationship between the presence and concentration of selected contaminants and the minimum well depth. Because, in all cases, wells are slotted all across the saturated zone, the well depth in Fig. 15 corresponds to the unsaturated zone
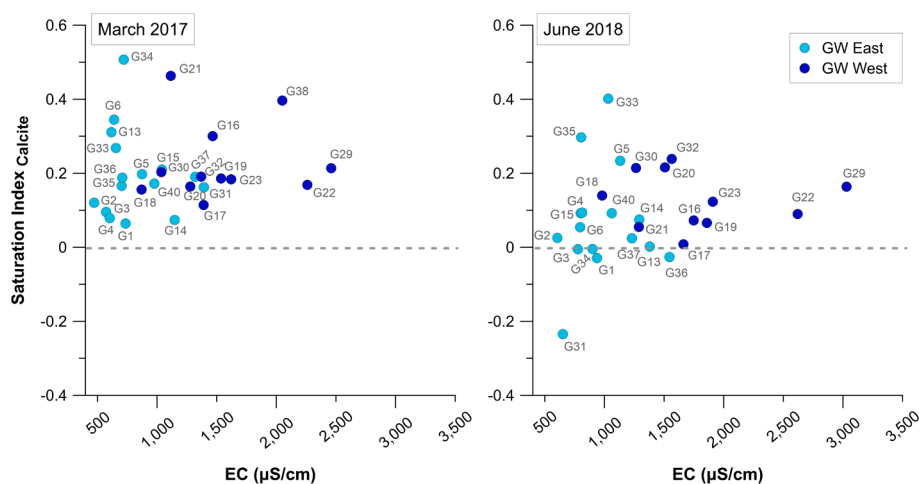
Fig. 13. Calcite saturation index and electrical conductivity in groundwater from the eastern sector (sky blue) and from the western sector (navy blue) of the VG aquifer. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 14. Relationship between chloride (mg/L) and δ^{18}O (‰) in groundwater (GW) from the eastern sector (sky blue) and from the western sector (navy blue) of the VG aquifer. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
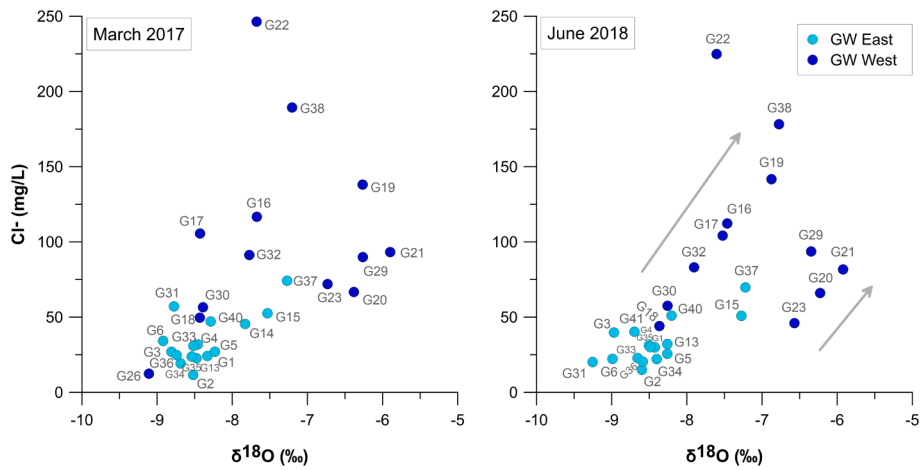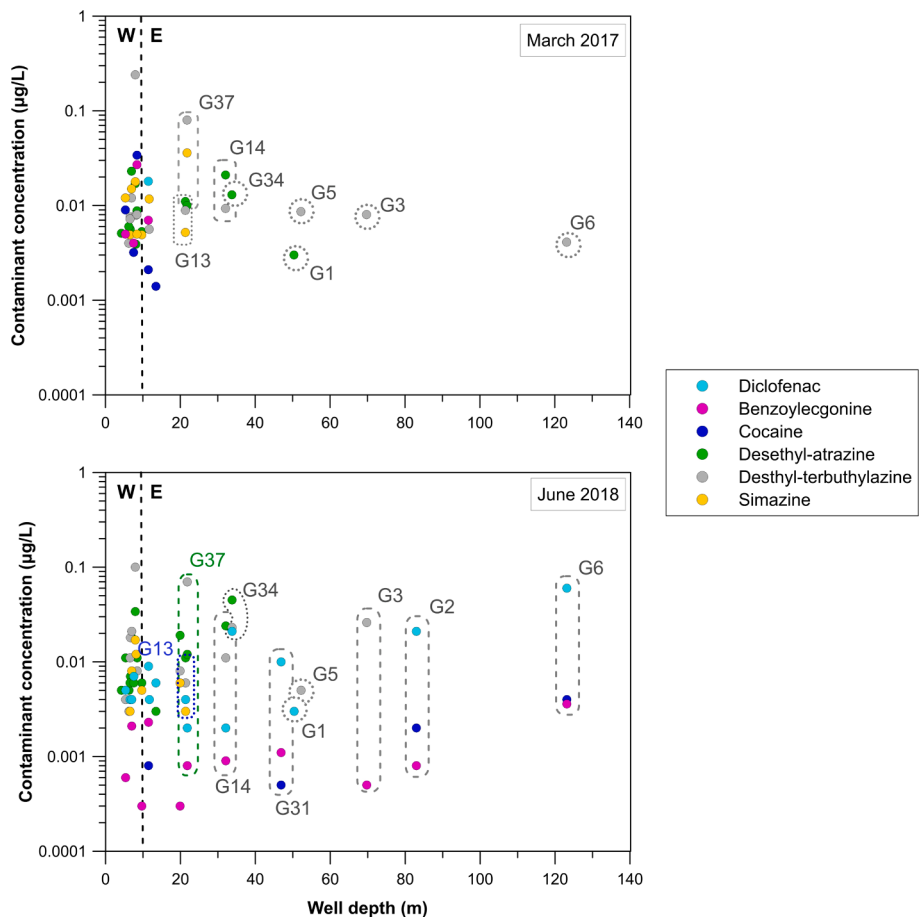

Fig. 15. Relationship between detected organic contaminant concentration in groundwater (μg/L) and depth of monitored wells. Dashed line indicates the eastern-western sectors limit.

thickness found at each well location. It can be observed that, in March 2017, most contaminants are detected in the shallowest wells, most of which are located in the western part of the aquifer (Fig. 3). In contrast, in the June 2018 monitoring campaign, selected pharmaceuticals become almost ubiquitous throughout much of the aquifer. The occurrence of desethyl-atrazine, desethyl-terbuthylazine and simazine between campaigns throughout the aquifer thickness does not change as significantly as that of pharmaceuticals.

The most remarkable variation observed in Fig. 15 relates to the detection of selected PhACs in June 2018 in the deepest wells, where they were not detected in March 2017; these were sampling points G6, G2, G3, G1, G31, G14, G34 and G37.

G6, G2 and G31 are located near the Monachil, Genil and Dílar Rivers, respectively (Fig. 1), where the aquifer consists of fluvial gravels and sands and has the highest transmissivity values. The isotopic composition (δ^{18}O) recorded in these wells is lighter in June, in line with

the oxygen-18 depletion of the aforementioned rivers (Fig. 8). SI$_{calcite}$ measured in these groundwater samples is lower (Fig. 13), suggesting recharge from surface fresh water. Therefore, in the case of these wells, recharging streams can be the path through which organic contaminants enter the groundwater. The Monachil and Dílar Rivers receive untreated wastewater discharges right before they enter the Granada plain, according to the basin authority (Fig. 4); two WWTP discharge into the Genil River before water enters the plain (Fig. S1). In June, surface water samples S7 (Monachil River), S8, S9 (Genil River) and S10 (Dílar River) showed detectable concentrations of diclofenac (from values below limit of quantification to 0.015 µg/L); S7, S8 and S9 showed detectable contents of benzoylecgonine (from values below limit of quantification to 0.005 µg/L) and S7 and S9 showed detectable contents of cocaine (below limit of quantification).

WWTPs in the Granada area include secondary treatment, which can be very effective in eliminating cocaine and benzoylecgonine, with removal rates above 88% (Huerta-Fontela et al., 2008), but are extremely unsuccessful in removing diclofenac (Kasprzyk-Hordern et al., 2009), which requires tertiary treatment (Alessandretti et al., 2021).

Sampling point G3, located in the southeastern part, shows a very low concentration of benzoylecgonine in June. Oxygen-18 depletion (Fig. 8) and a SI$_{calcite}$ decrease (Fig. 13) in the second monitoring campaign reflect the influence of freshwater recharge (either coming from riverbeds or from ditches that convey river freshwater for irrigation; Fig. S1). A very low concentration of the only pharmaceutical detected in G3 and no detectable pollutant concentration in sampling point G4, close to G3, in either of the two monitoring campaigns, can be attributed to the lower transmissivity of materials in this part of the aquifer, since pollution sources are not absent (Fig. 4). Being further away from riverbeds, these two wells are drilled in materials originating from alluvial fans deposited in the late Miocene (conglomerates, sands, silts and clays; Mateos et al., 2017). With a lower transmissivity, recharge water takes longer to reach the groundwater table and thus, the load of more degradable compounds (i.e., PhACs) can be reduced. As exposed, selected pharmaceuticals are potentially more mobile in the subsurface than triazines, and these are more susceptible to sorption processes. Generally, sorbed chemicals are less accessible to microorganisms, and, accordingly, sorption limits their degradation (Arias-Estévez et al., 2008).

Sampling point G36 did not show any detectable content of organic pollutants in any monitoring campaign (Fig. 12), and sampling point G5 showed a relatively low and similar concentration of triazines in both campaigns (Fig. 15), which are less mobile than the pharmaceuticals. This general absence of organic pollutants at these two points can be attributed to the fact that they are located in the northeastern part of the aquifer, where the hydraulic gradient is steeper (Fig. 3) due to a higher clay content (Mateos et al., 2017). In contrast, diclofenac was detected in June in G1, which is closer to a stream (Beiro River) in a zone where the aquifer materials become coarser and the hydraulic gradient decreases.

Sampling points G14, G34 and G37 showed a content of selected pharmaceuticals only in June (Fig. 15), but other PhACs were detected at these points in March (Fig. 12). This can be due to important and constant loads of wastewater coming from the northeastern boundary (Fig. 4). In addition, these wells are less deep than those located in the zone right next to the eastern boundary of the aquifer (G36, G5, G1, G35, G2) and that located in the south-east (G6, G4, G3, G31), which did not show any detectable content in PhACs in the March monitoring campaign (Fig. 12).

The shallower wells are more vulnerable to contamination. This can be due to the fact that pollutants persist in the soil and the unsaturated zone thanks to their organic matter and clay content, and undergo remobilization by the shallow water table (Sassine et al., 2016), which can be the case specially for those pollutants that are more hydrophobic, such as the triazines. The potential origin of pharmaceuticals in these wells, which are mainly located in the western zone, is irrigation, which often includes reclaimed wastewater rather than water recharge from riverbeds. This is because the aquifer recharges a gaining river in this sector and most urban wastewater discharges are close to the main stream (Fig. 4).

5. Conclusions

In this study, we provided the most extended dataset of the occurrence of pharmaceuticals and pesticides in water resources presented until now for the unconfined aquifer of the Granada Plain. The situation of the study area in terms of water pollution by these organic chemicals as well as an assessment of potential factors affecting their spread have been depicted.

A simple representation of the spatial distribution of the organic contaminants in the study area (Fig. 12) is not easy to interpret. The wide variety of factors influencing the occurrence of these pollutants makes spatial and seasonal analysis a challenging task. Physicochemical and hydrochemical parameters along with environmental stable isotopes have been used to define the hydro(geo)logical context of the study area during the monitoring campaigns. This has contributed to the understanding of the spatial and seasonal distribution of the contaminants.

In this study, four factors have been highlighted for their influence on the occurrence of organic pollutants: (I) variability of unsaturated zone thickness; (II) river-groundwater hydraulic connection; (III) hydraulic gradient; and (IV), the anthropogenic factor determining the period of contaminant release throughout the year and wastewater management practices. The unsaturated zone thickness plays a powerful protective role in relation to groundwater contamination, namely, the presence of selected pharmaceuticals in groundwater was related to the shallowest water table (<15 m) in the first monitoring campaign (March 2017). However, the vadose zone is not an insurmountable obstacle if water recharge from the surface increases. An increase of stream flow potentially causing aquifer water recharge did not result in a dilution of emerging contaminants as initially expected. Instead, it promoted their widespread distribution across the alluvial aquifer, resulting in the detection of selected pharmaceuticals in wells as deep as 123 m. As a matter of fact, pollution transfer to deeper wells due to water recharge took place in the southeastern part of the aquifer, where transmissivity values are high and where groundwater has a better quality and, therefore, where groundwater is extracted for urban supply. Water management should focus on eliminating groundwater quality threats such as untreated wastewater discharges and its use for irrigation, and should consider further treatment in existing WWTPs. Concentration of organic contaminants in wells situated in the northeastern part, with less permeable materials and a greater hydraulic gradient, remain very low or under detection limits. In essence, when the aquifer recharge process from the surface is delayed (either by a thick vadose zone or due to the presence of poorly permeable materials), pollutants that are more susceptible to degradation do not reach the water table at detectable concentrations.

Finally, the importance of the anthropogenic factor cannot be ignored, as evidenced by the opposite seasonal tendency regarding frequency of detection of pharmaceuticals and herbicides. Typical pesticide application periods can explain the appearance of herbicides in March and their frequency detection decrease in June. The increase of urban water demand (potentially due to growth of tourism in summer) can also explain a higher frequency of detection of pharmaceuticals and drugs of abuse in June in both surface water and groundwater. Intensification of irrigation should also be considered as a potential path of entry of urban organic contaminants. Treated and untreated urban wastewater is released to streams, from which water is diverted for irrigation, and also discharged directly into irrigation channels and ditches.

The hydrodynamic context in the study area drives the greatest changes between seasons in the southeastern part of the aquifer, where

transmissivity values are greater. Further research will focus on these zones and will require conducting more frequent monitoring work over time to better characterize this phenomenon. Research funds will be more efficiently spent by monitoring just the most frequent compounds detected in this work.

CRediT authorship contribution statement

M.I. Llamas: Writing – original draft, Investigation, Writing – review & editing, Visualization, Formal analysis. **P. Jiménez-Gavilán:** Conceptualization, Methodology, Supervision, Data curation. **J.A. Luque-Espinar:** Methodology, Data curation. **J. Benavente-Herrera:** Methodology, Data curation, Supervision. **L. Candela:** Writing – review & editing, Supervision. **M. Sanmiguel-Martí:** Methodology, Data curation. **J. Rambla-Nebot:** Methodology, Data curation. **J.L. Aranda-Mares:** Methodology, Data curation. **I. Vadillo-Pérez:** Conceptualization, Methodology, Funding acquisition, Project administration, Supervision, 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.jhydrol.2022.127791.

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