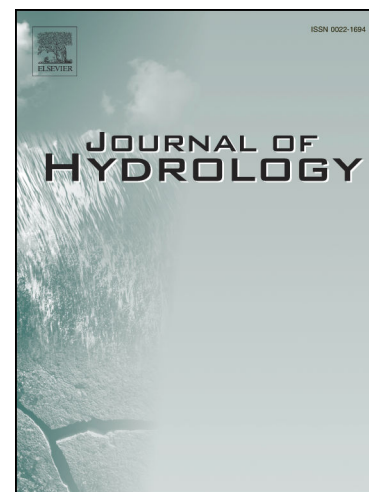


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Research papers

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

M.I. Llamas, P. Jiménez-Gavilán, J.A. Luque-Espinar, J. Benavente-Herrera, L. Candela, M. Sanmiguel-Martí, J. Rambla-Nebot, J.L. Aranda-Mares, I. Vadillo-Pérez

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

4

5 Llamas, M.I.¹, Jiménez-Gavilán, P.¹, Luque-Espinar, J.A.^{2,3}, Benavente-Herrera, J.², Candela,
6 L.⁴, Sanmiguel-Martí, M.⁵, Rambla-Nebot, J.⁵, Aranda-Mares, J.L.⁵, Vadillo-Pérez, I.^{1*}

7

8 ¹ : Group of Hydrogeology, Department of Geology, Faculty of Science, University of Málaga, 29071
9 Málaga, Spain, mllamas@uma.es, pgavilan@uma.es, vadillo@uma.es

10 ²: IGME (Instituto Geológico y Minero de España), Granada Office. ja.luque@igme.es

11 ³: Department of Geodynamics, Faculty of Sciences, University of Granada, 18071 Granada, Spain.

12 ja.luque@igme.es, jbenaven@ugr.es

13 ⁴: IMDEA-Water, 28805 Alcalá de Henares and IUACA, 03690 Alicante, Spain; lucila.candela@imdea.org

14 ⁵: IPROMA S.L. Camino de la Raya, 34. Castellón. jaranda@iproma.com

15 * Corresponding author: at Group of Hydrogeology, Department of Geology, Faculty of Science, University
16 of Málaga, 29071 Málaga, Spain. E-mail address: vadillo@uma.es

17

18 **Abstract**

19 The anthropogenic organic contaminants contemplated in the environmental legislation,
20 as well as those of emerging concern, threaten the quality of water resources to a degree that
21 remains largely unknown. Contaminant exposure in the aquatic environment is a crucial
22 element if a full understanding of the risk is pursued. There are still many uncertainties about
23 the occurrence of organic pollutants and behavior in the hydro(geo)logical media in large scale
24 areas. The case study of the unconfined aquifer of the Granada Plain (approximately 200 km²)
25 is presented here. Two surface and groundwater monitoring campaigns were conducted (March
26 2017 and June 2018). In total, 41 out of 171 target organic pollutants were detected, at least
27 once: 17 pharmaceuticals or drugs of abuse, 21 pesticides or their metabolites and three
28 polyaromatic hydrocarbons. In addition, physico-chemical parameters were measured during
29 the monitoring campaigns and hydrochemical parameters and stable isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$)

30 were analyzed. Statistical tests confirmed the significance of seasonal changes for some of
31 these parameters (e.g., EC, Cl⁻, F⁻, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$), revealing the influence from snowmelt water
32 input on streams and the intensification of irrigation. In March 2017, the group of pesticides
33 (largely represented by triazines) predominated, whereas the frequency of detection of
34 pharmaceuticals increased substantially in June 2018. Results suggest four main factors
35 affecting the spatial and seasonal variation of organic pollutants in the aquifer: the
36 anthropogenic factor determining the period of contaminant release throughout the year
37 (pesticide application period and growth of tourism) along with irrigation practices that include
38 reclaimed wastewater; unsaturated zone thickness; hydraulic gradient and river-groundwater
39 hydraulic connection. The latter can be especially important in the case of those contaminants
40 whose main path of entry into the aquatic environment occurs through wastewater discharge
41 into streams (i.e., pharmaceuticals).

42

43 **Key words:** Pharmaceuticals, pesticides, detrital aquifer, seasonal variation, unsaturated zone,
44 recharge process.

45

46 1. Introduction

47 A contaminant of emerging concern (CEC) is known as such not only because it has
48 been recently considered to cause known or suspected adverse ecological or human health
49 effects (Stuart *et al.*, 2012) but also because they remain largely unregulated in the field of
50 water policy (Daughton, 2004). Nonetheless, the importance of learning more about their
51 occurrence, harmful potential and environmental behavior, has been recognized and highlighted
52 by institutions and the scientific community. According to Directive 2013/39/EU (European
53 Parliament and of the Council, 2013), the European Commission must establish a Watch List
54 that includes substances that can be of concern and for which information must be gathered. To
55 date, three Watch Lists have been set out (European Commission, 2020) which include
56 substances that are essentially pharmaceuticals and pesticides. Similarly, a Watch List for
57 pollutants in groundwater, including emerging contaminants, has also been demanded
58 (European Commission, 2014; Lapworth *et al.*, 2019).

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

67 The potential adverse effects of emerging pollutants to human health or to ecosystems
68 have also been researched and reviewed (López-Pacheco *et al.*, 2019; Lei *et al.*, 2015; Pereira
69 *et al.*, 2015). However, in order to fully understand the risk that CECs may entail, the exposure
70 must be defined, and this is why hydrogeological studies are essential (Mas-Pla, 2018). Large-
71 scale studies are very valuable to understand the spatial occurrence and trends of CECs, and
72 will help build a foundation for future regulation. Yet these studies are not as frequently
73 conducted as they should (Bunting *et al.*, 2020). Furthermore, the spatial distribution of
74 anthropogenic organic contaminants is challenging to assess, as it can be affected by several
75 factors such as the spatial and temporal distribution of pollution sources. Since wastewater
76 treatment is not fully successful at eliminating CECs (Carballa *et al.*, 2004; Carballa *et al.*,
77 2005), wastewater discharge into streams acts as the main path of entry into the aquatic
78 environment, which is the reason why emerging contaminant research has mainly focused on
79 surface water (Stuart *et al.*, 2012). Other factors need to be considered: the influence of the
80 hydraulic context on CECs occurrence was observed by Corada *et al.* (2017) who compared
81 periods of droughts and extreme rainfall events; Lutri *et al.* (2020) determined the relationship
82 between the presence of glyphosate and its main metabolite and shallowest water table and low
83 flow velocity. The physico-chemical properties of the pollutants themselves can grant them
84 different environmental behaviors (Massmann *et al.*, 2006; Schaffer and Licha, 2015; Martínez-
85 Hernández *et al.*, 2016). Llamas-Dios *et al.* (2020) pointed out the potential role of hydraulic
86 infrastructure on spatial distribution of hydrophilic CECs (i.e. pharmaceuticals).

87 In this study we present the spatial distribution and seasonal variation of CECs and other
88 regulated organic pollutants in water resources of the *Vega de Granada* aquifer (hereafter VG

89 aquifer; *vega* means irrigated plain in Spanish), an alluvial aquifer of 200 km², approximately.
90 One-hundred and seventy-one organic pollutants were analyzed including pharmaceuticals,
91 pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and
92 brominated diphenyl ethers (BDEs). Data interpretation focused on the distribution of
93 pharmaceuticals, pesticides and their metabolites, according to their higher frequency of
94 detection, as it will be seen in following sections. Two monitoring campaigns were carried out in
95 order to assess the importance of aquifer recharge processes associated with seasonal
96 changes (natural and anthropogenic).

97 The VG aquifer is an alluvial aquifer covered by agricultural lands and urban areas
98 demanding an increasing volume of water resources, from surface streams and the subsoil.
99 Human activities have led to a general increase of salinity (Castillo *et al.*, 2010) and high nitrate
100 contents in groundwater due to decades of fertilizer use (Castillo, 2005; Rodriguez-Galiano *et al.*,
101 2018) and to a decrease of water recharge and renewal rates (Castillo *et al.*, 2010).
102 Microbiological contamination has also proven to be a sanitary problem in this region (Castillo
103 and Ramos-Cormenzana, 2002).

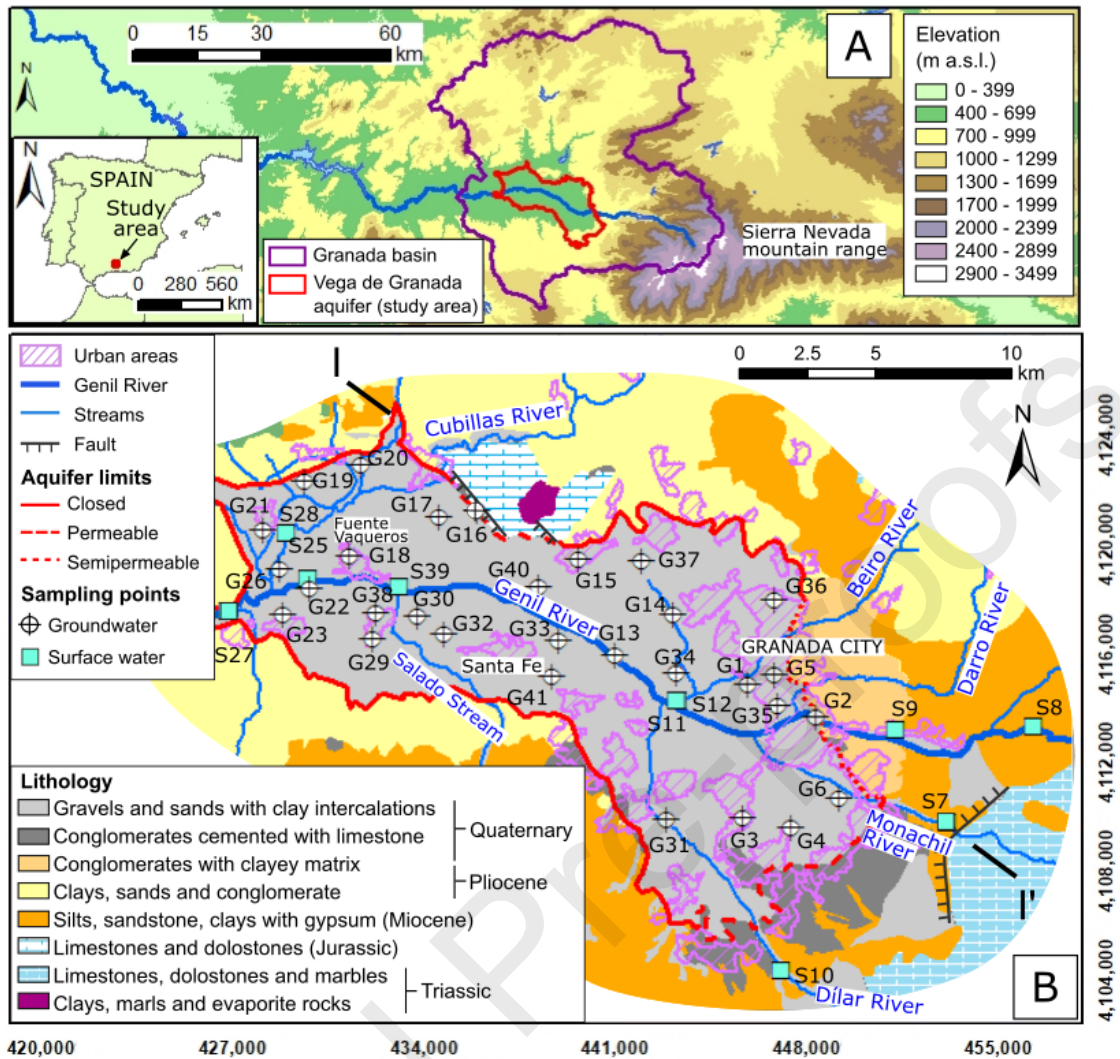
104 Luque Espinar *et al.* (2015) conducted a study on the distribution and seasonal variation
105 of six CECs in water resources of Granada city metropolitan areas, observing water pollution by
106 pharmaceutical active compounds (ibuprofen, paracetamol, caffeine and pantoprazole) and
107 even affection on the crops, which are usually irrigated with wastewater. Luque-Espinar and
108 Chica-Olmo (2020) observed an important affection by wastewater in the entire aquifer;
109 amoxicillin, caffeine, paracetamol and ibuprofen were detected in collected vegetables. As
110 mentioned, in the present study the number of target pollutants to be analyzed in water
111 resources has been expanded.

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

119 hydrogeological characteristics of the aquifer, hydrodynamic context, physico-chemical
120 properties of the pollutants, human practices) on the spread of organic pollutants in the VG
121 aquifer.

122 **2. Study area**

123 The Vega de Granada (VG) plain extends over 200 km² and is located in the south of the
124 Iberian Peninsula, in Spain (Fig. 1). The VG Plain is at the center of the Upper Genil River
125 catchment (2,950 km²), also known as the Granada basin. It is the largest water consumption
126 zone within the catchment area, meeting the demands of 120 km² of irrigation lands and
127 550,000 inhabitants, approximately (Castillo et al., 2010). The Genil River starts in the Sierra
128 Nevada Mountain Range on the east and flows through the plain in a westerly direction, where it
129 is joined by several tributaries. The elevation of the plain is about 550 m a.s.l., the Sierra
130 Nevada Mountains reaching 3,470 m a.s.l. The average temperature in the plain is around 15-
131 16 °C whereas that of the Sierra Nevada ranges from 5 to 6°C at an elevation of 2,550 m a.s.l.
132 Mean annual precipitation is 490 mm/year in the plain and about 1,000 mm/year in the upper
133 mountains (Kohfahl et al., 2008).



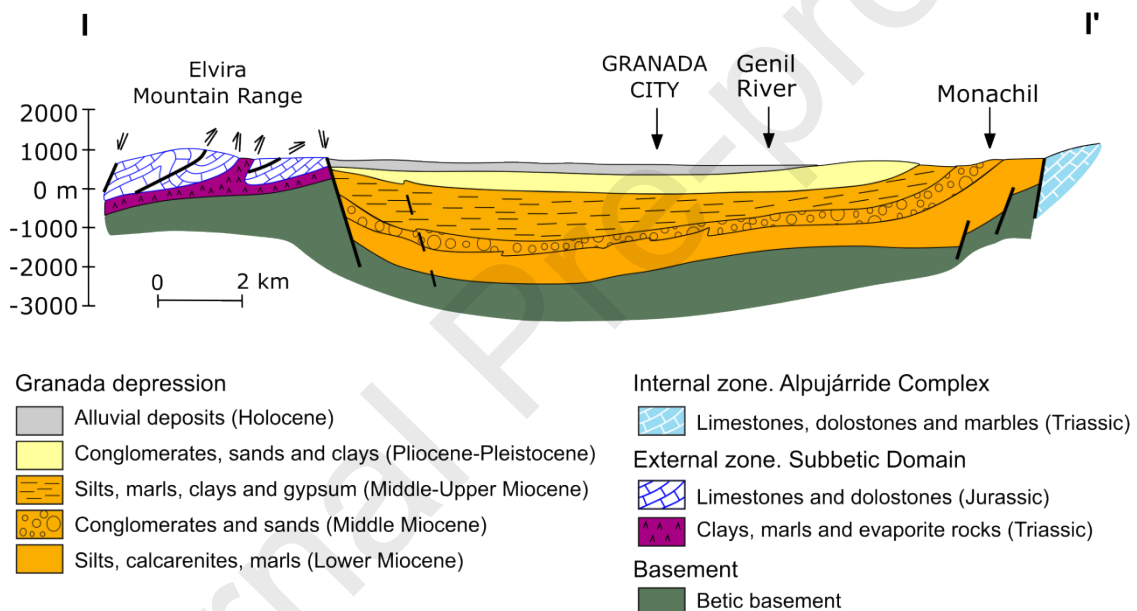
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135 **Fig. 1.** Location, topographic map (A; IAECA, 2019) and lithological map (modified from Castillo-Martín,
 136 1986; IGME, 1990) of the study area with sampling points (B).

137

138 The Granada basin (Fig. 1) consists of an outcrop of Neogene to Quaternary sediments
 139 overlying the NE-SW trending contact between the External and Internal Zones of the Betic
 140 Cordillera. The sequence of the sedimentary materials is over 2 km thick in some areas. Uplift of
 141 the cordilleras that started in the late Miocene generated normal faults that defined the basin
 142 limits and caused the deposition of alluvial and delta fans along the edges. The aquifer
 143 corresponds to the Holocene (Quaternary) detritic sediments filling the tectonic depression,
 144 which presents a sedimentary multilayered structure with levels of gravels, sand, silt and clay,
 145 as a result of the coalescence between river sedimentation and that of the alluvial fans. Aquifer
 146 thickness reaches up to 250 m in the center part (Mateos et al., 2017). Low permeability

147 Neogene and Quaternary materials showing variable lithology bound the VG aquifer, except for
 148 a Jurassic carbonate outcrop located in the north (DPG-IGME, 1990). The latter consists of
 149 limestones and dolostones overlying a Triassic evaporitic basement. Miocene (Neogene)
 150 materials form the basement of the alluvial sediments of the aquifer (DPG-IGME, 1990). The
 151 general Neogene sedimentary sequence is composed of calcarenites, terrigenous sediments
 152 and evaporites (Kohfahl *et al.*, 2008; Fig. 2). The Holocene VG aquifer boundaries are closed,
 153 except for those in contact with the Jurassic carbonates and those in contact with coarse-
 154 grained upper Pliocene-lower Pleistocene materials at the eastern boundary and with
 155 Quaternary alluvial fan materials in the southeast. The VG aquifer fine-grained substratum is
 156 impervious due to its content in clays and silts (Luque-Espinar *et al.*, 2002).



157

158

159 **Fig. 2.** Geological cross-section modified from IGME (2009). I-I' location indicated in Fig. 1.

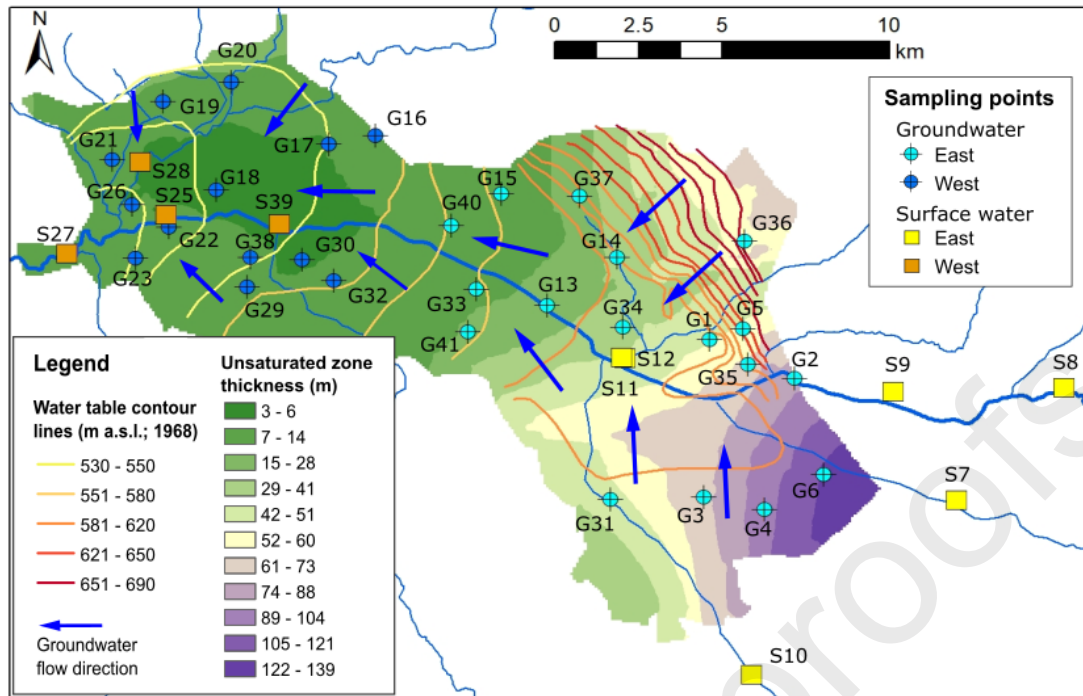
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161 Transmissivity of the VG aquifer ranges between 100 and 40,000 m²/day, with an
 162 average of 4,000 m²/ day (Castillo *et al.*, 2010). Along the central axis of the aquifer and in the
 163 southeastern part, in zones close to the Genil River and the Monachil and Dílar Rivers, the
 164 aquifer consists mainly of fluvial gravels and sands. Thus, the highest transmissivity values are
 165 observed in these zones. Coarse sediments with thicknesses of up to 150 m have been
 166 recorded at the central zone of the aquifer. Clay content increases towards the boundaries and

167 a minimum clay content of 80% has been estimated in the northeastern part of the aquifer
168 (Mateos *et al.*, 2017) where the steepest hydraulic gradient is observed (Fig. 3).

169 Average renewable water resources of the VG aquifer are estimated to be 160 hm³/ year
170 (Castillo *et al.*, 2010). Aquifer water recharge comes mainly from surface runoff generated in the
171 Granada basin. Nevertheless, the main recharge area is located in the southeastern sector,
172 where most tributaries join the main riverbed (Chica-Olmo *et al.*, 2014). Thus, water recharge
173 from surface water infiltration takes place essentially thanks to infiltration from the Genil, Dílar
174 and Monachil Rivers (CHG, 2021; Fig. 1). Infiltration of surface runoff is strongly driven by
175 irrigation through a dense network of irrigation channels and ditches that takes up part of this
176 surface water. This water input is estimated to be 126 hm³/ year. Rain infiltration over the
177 permeable surface of the aquifer adds 24 hm³/ year, and contribution from adjacent aquifers is
178 around 10 hm³/ year (Castillo *et al.*, 2010), which is likely to occur mainly at the southeastern
179 boundary of the aquifer, near to the more permeable carbonate rocks (Kohfahl *et al.*, 2008).
180 Aquifer discharge occurs, on the one hand, through natural discharge in the western sector of
181 the aquifer, downstream from the town of Fuente Vaqueros, through springs and diffuse
182 sources towards the Genil and Cubillas Rivers (IGME, 1990). The average value of this output
183 has been estimated at 110 hm³/ year. On the other hand, net groundwater abstraction through
184 wells accounts for the remaining 50 hm³/year, 85% for agricultural use and 15% for urban water
185 supply (Castillo *et al.*, 2010).

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



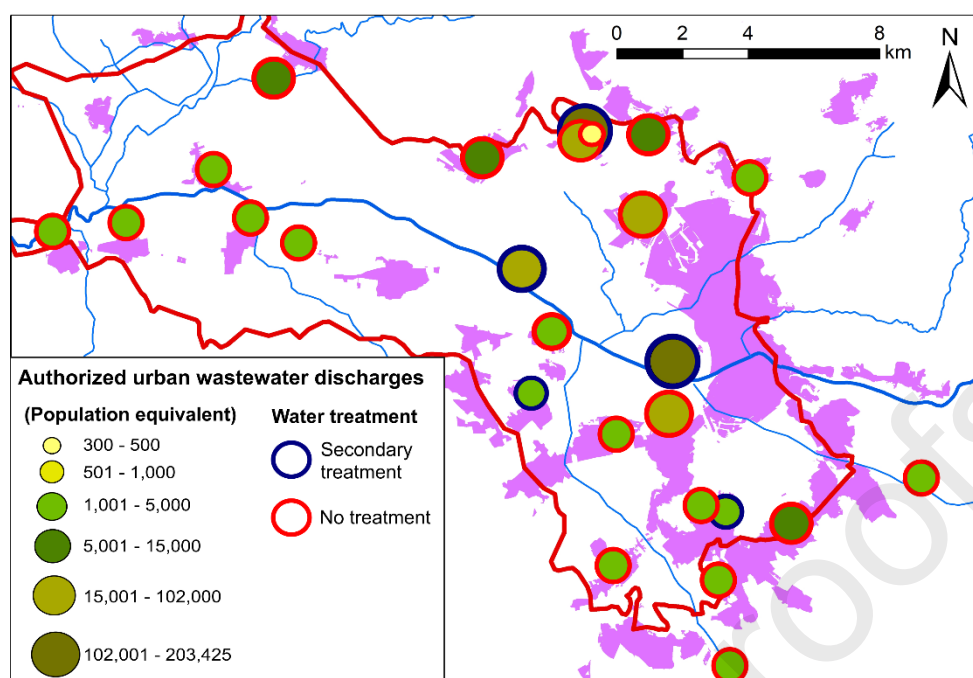
192

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

196

197 There are two wastewater treatment plants (WWTP) treating wastewater from the
 198 Granada area (Fig. S1). In these facilities, 42 hm³ and 37 hm³ of wastewater was treated in
 199 2017 and in 2018, respectively. Purification processes consist of preliminary treatment, a
 200 primary sedimentation process, secondary biological treatment and secondary sedimentation.
 201 Treated and untreated urban wastewaters are directly released into ditches of the irrigation
 202 network or into riverbeds, from which water is also used for irrigation (Robles-Arenas *et al.*,
 203 2012). The location and magnitude of urban wastewater discharge permitted by the basin
 204 authority can be seen in Fig. 4.

205



206
207 **Fig. 4.** Urban wastewater discharge into the environment approved by the basin authority (CHG, 2013).

208 3. Materials and Methods

209 3.1. Water sampling and measurement of physico-chemical parameters

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

217 Water samples were filtered using a 0.45 μm Millipore® filter (Merck KGaA, Darmstadt,
218 Germany). Sterile high-density polyethylene bottles (120 mL) sealed with inverted cone caps
219 were used to store water samples for hydrochemical and isotopic analyses. Water samples
220 used for organic contaminants analysis were stored in sterile amber glass bottles (1L) with
221 Teflon caps. Bottles were rinsed before sampling, carried in an ice-filled cool-box and stored in
222 a fridge ($< 4\text{ }^{\circ}\text{C}$) until analysis. Physico-chemical parameters (pH, temperature, electrical
223 conductivity, redox potential and dissolved oxygen) were measured with a portable multi-
224 parameter probe (Hach-Lange HQ40d; Hach, Loveland, CO, USA).

225 3.2. Water major and minor ions and isotopic analysis

226 Major and minor water ions were determined by ion chromatography using a Metrohm
227 881 Compact IC Pro (HPLC). Water stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$ (‰; Vienna Standard Mean
228 Oceanic Water), were determined in a Picarro Water Isotope Analyzer L2120i (laser
229 spectroscopy). $\delta^{13}\text{C}$ from dissolved inorganic carbon (‰; Vienna Pee Dee Belemnite) was
230 determined in a Picarro Carbon Isotope Analyzer G1111i-CRDS. Hydrochemical and isotope
231 analyses were conducted at the laboratory of the Centre for Hydrogeology of the University of
232 Malaga. The PHREEQC code was used to calculate the state of saturation (saturation index) for
233 calcite (Parkhurst & Appelo, 1999).

234 3.3. Organic contaminant analysis

235 Water samples were analyzed for 171 organic pollutants (Table S1). Analyses of
236 pharmaceutically active compounds (PhACs), abuse drugs and polar pesticides and
237 metabolites, were performed by means of on-line solid-phase extraction (SPE) followed by
238 liquid chromatography-triple quadrupole mass spectrometry (HPLC-QqQ-MS/MS) (Shoemaker,
239 2015; Stoob *et al.*, 2005). Non-polar compounds and some priority substances (PAHs, PCBs,
240 organochlorine and organophosphorus pesticides, triazines and brominated diphenyl ethers)
241 were analyzed by gas chromatography coupled to mass spectrometry (GC-MS), preceded by
242 stir bar sorptive extraction (SBSE) (León *et al.*, 2003; 2006). Organic compound analysis was
243 conducted at the IPROMA laboratory (Castellón, Spain).

244 3.4. Statistical analysis

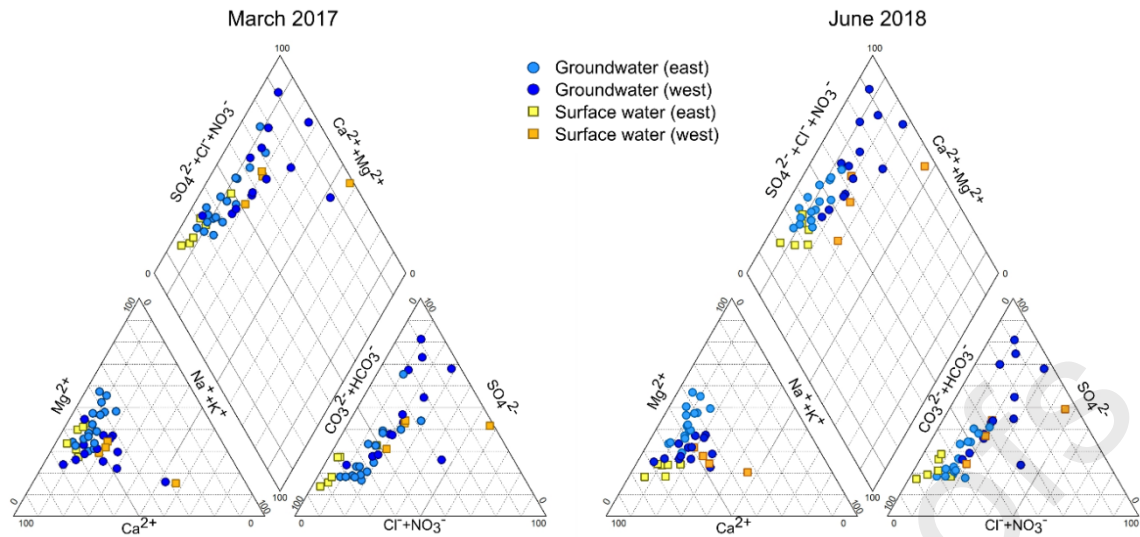
245 To evaluate the statistical significance of seasonal change of surface water and
246 groundwater, the paired sample *t* test was used. The latter was applied to physico-chemical and
247 hydrochemical parameters. The *t* test requires the differences between paired observations to
248 be normally distributed (Helsel *et al.*, 2020). To check the normal distribution of differences, the
249 Shapiro-Wilk test was used. For datasets that do not follow a normal distribution, the non-
250 parametric Wilcoxon signed-rank test was applied (Helsel *et al.*, 2020). The analyses were
251 performed using the 'stats' package in R software (R Core Team, 2020). If the obtained *p-value*

252 is below 0.05, the null hypothesis stating that the two compared groups do not differ significantly
253 was rejected.

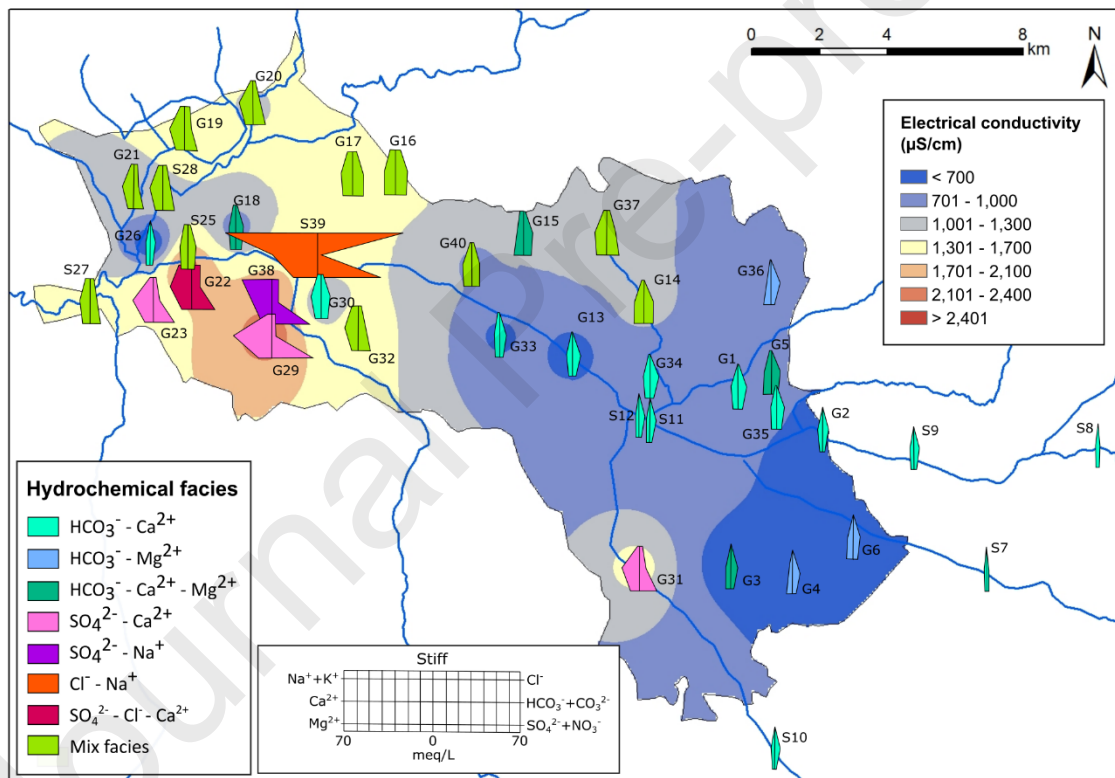
254 **4. Results and discussion**

255 *4.1. Surface and groundwater hydrochemical composition*

256 Descriptive statistics of measured physico-chemical parameters and hydrochemical
257 results are available in the Supplementary Material section (Tables S2 and S3). A spatial
258 variability of hydrochemical characteristics is observed in the study area regarding both surface
259 water and groundwater (Fig. 5; Fig. 6). Calcium and magnesium bicarbonate low-mineralized
260 type water is predominant in the eastern part, potentially as a consequence of water input
261 coming from the Sierra Nevada Mountain Range through riverbeds. In contrast, mixed facies
262 with a higher level of mineralization are most commonly found in the western part, indicating
263 different factors affecting water quality other than rock-water interaction (i.e., impact of human
264 activities). Sulphate-sodium, chloride-sodium and sulphate-calcium facies near the southern
265 aquifer limit reflect the influence of the evaporitic materials from the Miocene deposits. The
266 electrical conductivity (EC) mean value was higher in the western sector in both campaigns: a
267 mean value of $1,453 \pm 538 \mu\text{S/cm}$ was recorded in groundwater in the western sector in March
268 2017 ($1,767 \pm 567 \mu\text{S/cm}$ in June 2018), whereas a mean value of $824 \pm 266 \mu\text{S/cm}$ was
269 recorded in groundwater from the eastern sector in March 2017 ($977 \pm 255 \mu\text{S/cm}$ in June
270 2018). As regards surface water, a mean value of $1,162 \pm 166 \mu\text{S/cm}$ was recorded in the
271 western sector in March 2017 ($909 \pm 490 \mu\text{S/cm}$ in June 2018) and a mean value of 333 ± 69
272 $\mu\text{S/cm}$ was recorded in the eastern sector in March 2017 ($176 \pm 51 \mu\text{S/cm}$ in June 2018).
273 Hence, in terms of temporary variation, groundwater EC values were significantly higher ($p <$
274 0.05 ; see Table S4) in June than in March. However, fluoride is the only ion increasing its
275 concentration significantly in groundwater in June. In contrast, surface water EC values were
276 significantly lower in June than in March. This EC decrease was statistically significant only in
277 the eastern sector probably because the streams are influenced in the west by groundwater
278 quality. Ca^{2+} , Mg^{2+} , Na^{2+} , HCO_3^- , SO_4^{2-} , and Cl^- diminish significantly ($p < 0.05$) in surface water
279 in the eastern sector, which is consistent with the EC decrease. However, surface and
280 groundwater types remain very similar in both monitoring campaigns, as observed in Piper
281 diagrams (Fig. 5).



282

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

284

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

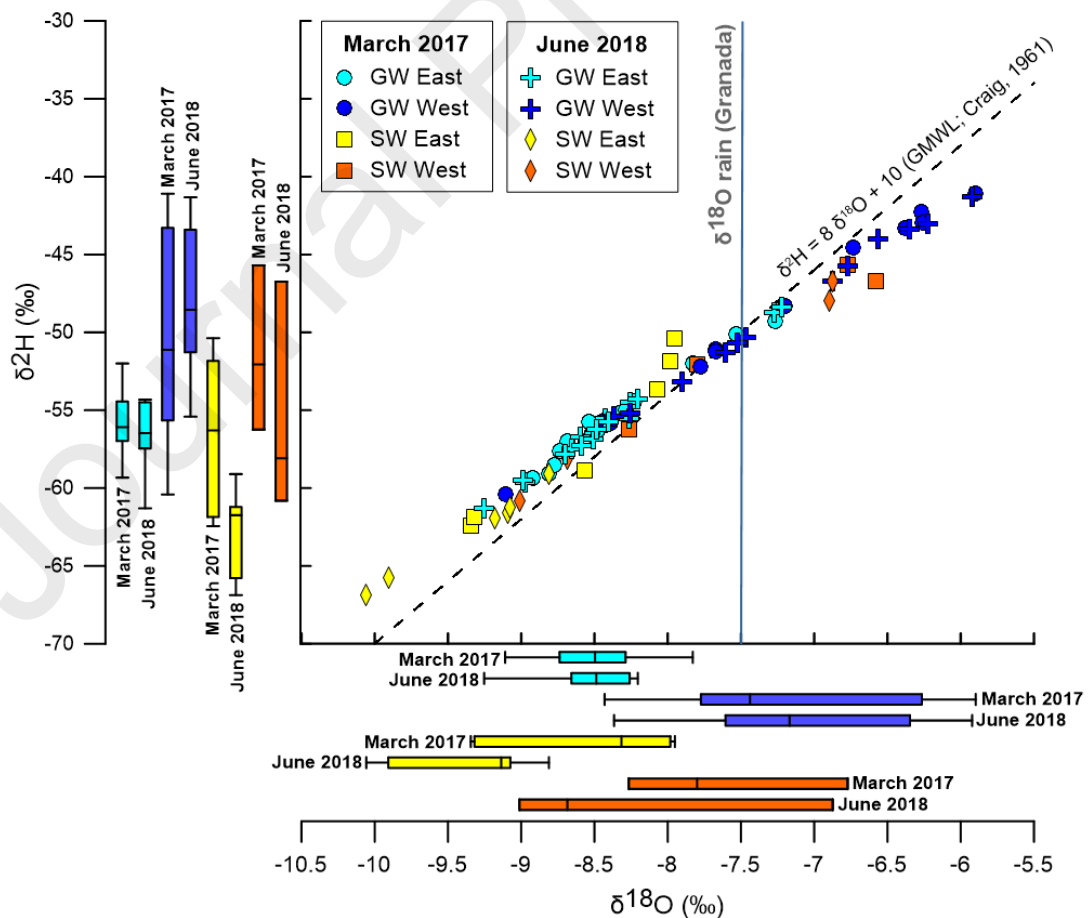
289

290 Nitrate concentration values in groundwater surpass the threshold value (50 mg/L;
 291 European Parliament and the Council of the European Union, 2006) in both sectors, although a

292 higher mean value is determined in the western sector, indicating worse water quality. Nitrate
 293 concentrations have been high for decades in the VG aquifer as a result of a fertilizer input for
 294 crops and low renewal rates (Castillo *et al.*, 2010; Plata-Bedmar and Greciano-González, 2018).
 295 No seasonal change in nitrate concentration has been statistically significant ($p > 0.05$).

296 4.2. Surface and groundwater stable isotopes

297 Groundwater from the eastern sector is more depleted in oxygen-18 (mean = $-8.4 \text{ ‰} \pm$
 298 0.5 in both monitoring campaigns) and deuterium (mean = $-55.5 \text{ ‰} \pm 2.9$ in March 2017 and -
 299 $56.0 \text{ ‰} \pm 3.5$ in June 2018) than groundwater in the western sector ($\delta^{18}\text{O}$ mean value = -7.4 ‰
 300 ± 1.0 in March 2017 and $-6.6 \text{ ‰} \pm 2.3$ in June 2017; $\delta^2\text{H}$ mean value = $-51.3 \text{ ‰} \pm 5.3$ in March
 301 2017 and $-55.2 \text{ ‰} \pm 7.5$ in June 2018; Fig. 7). Oxygen-18 spatial variation can be observed in
 302 Fig. 8 for both monitoring campaigns. Similar isotopic signals of groundwater in the eastern
 303 sector and surface water coming from the east reveal the significance of these streams as a
 304 source of groundwater. Little recharge contribution from rainwater is estimated, since its $\delta^{18}\text{O}$
 305 signal is -7.5 ‰ (Delgado-Huertas *et al.*, 1991).



306

307 **Fig. 7.** Water stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$ in ‰) of monitored surface water and groundwater of the VG
308 aquifer in both monitoring campaigns and average $\delta^{18}\text{O}$ of rain water in Granada (Delgado-Huertas *et al.*,
309 1991).

310

311 Although mean values do not change substantially in groundwater between the two
312 monitoring campaigns, some difference can be observed. In the June 2018 campaign, few more
313 extreme values were recorded. More depleted oxygen-18 values were recorded near the
314 southeastern boundary of the aquifer and slightly more enriched oxygen-18 values were
315 observed in the western part (Fig. 8). This isotope enrichment suggests an intensification of
316 irrigation during this warmer season. Evaporation from irrigation return flows can cause
317 enrichment in oxygen-18 in groundwater (Urresti-Estala *et al.*, 2016). On the other hand,
318 surface water in the east was significantly more depleted in this isotope (Fig. 7, Fig. 8) in June
319 2018 (mean = $-9.4 \text{ ‰} \pm 0.5$) than in March 2017 (mean = $-8.5 \text{ ‰} \pm 0.7$). During spring and
320 summer, these rivers receive meltwater from the Sierra Nevada (Fig. 1) with lighter $\delta^{18}\text{O}$
321 because of the high-altitude precipitation. River-aquifer interactions in the east can cause
322 oxygen-18 depletion in groundwater near the southeastern sector where the rivers lose water
323 towards the aquifer. Additionally, the statistical analysis showed that the seasonal $\delta^{18}\text{O}$ variation
324 was only significant in the case of surface water in the eastern sector ($p < 0.05$).

325

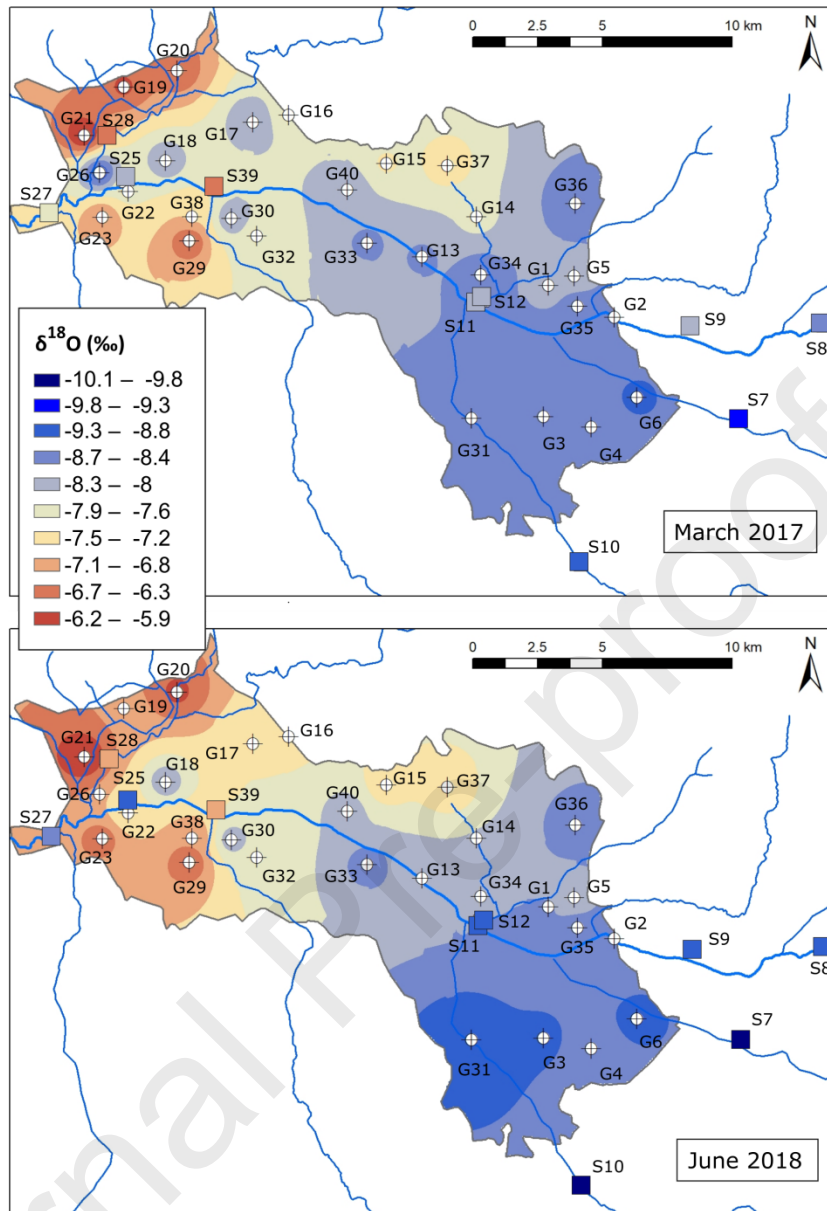


Fig. 8. $\delta^{18}\text{O}$ (‰) groundwater contour lines and $\delta^{18}\text{O}$ (‰) of surface water sampling points (squares).

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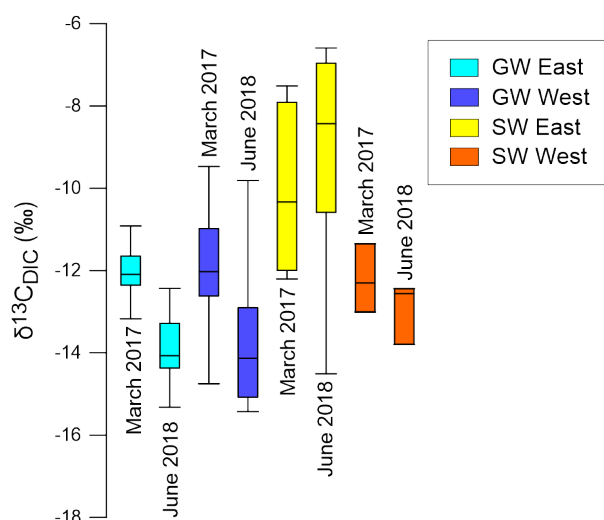
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Surface water from rivers flowing from the east was also more enriched in carbon-13 in June than in March (Fig. 9). An increase in $\delta^{13}\text{C}$ can indicate CO_2 removal from water by photosynthesis, which is more intense in warmer months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



337

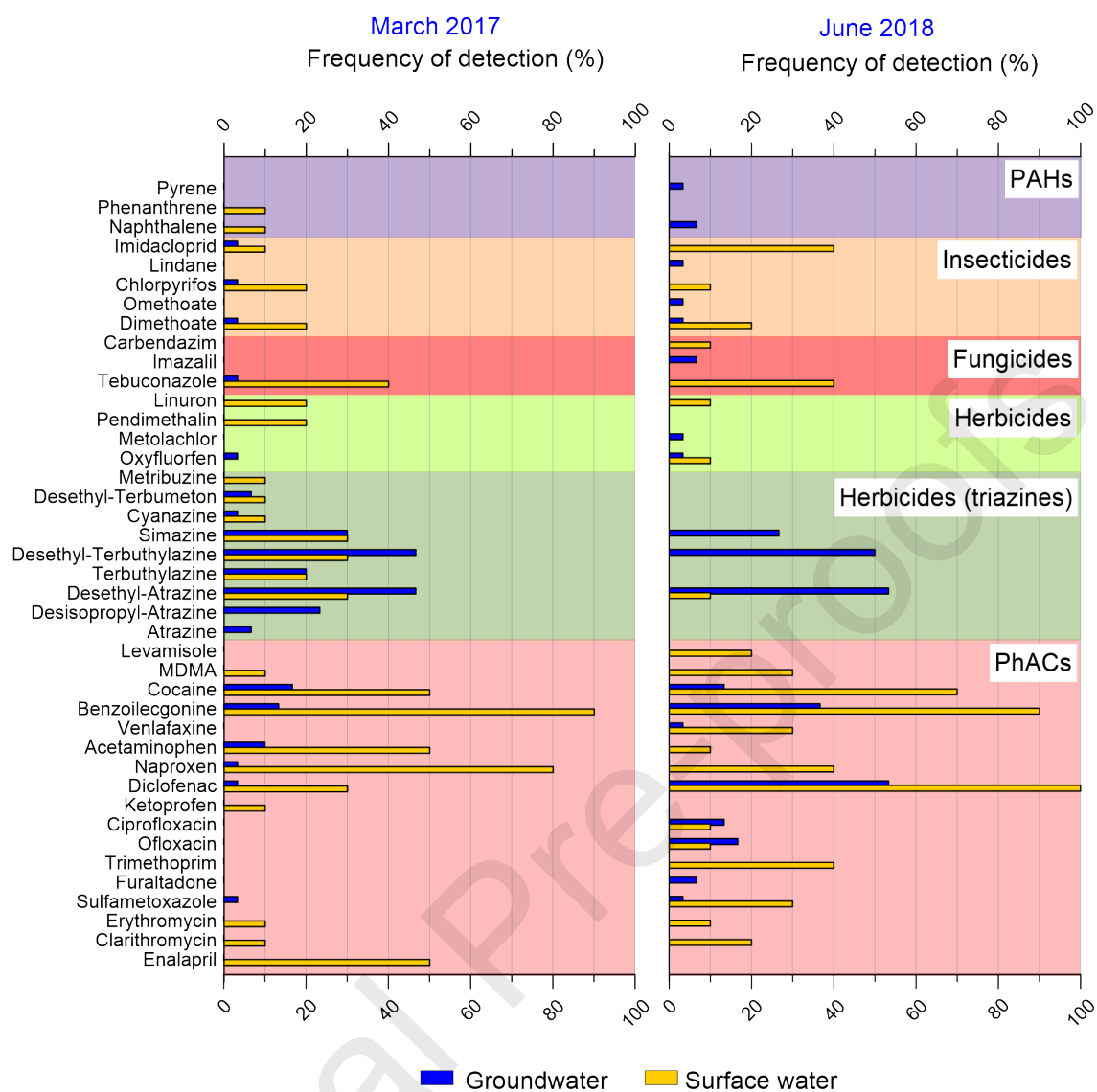
338 **Fig. 9.** $\delta^{13}\text{C}_{\text{DIC}}$ (‰) of monitored surface water and groundwater in the two monitoring campaigns.

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

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

345 4.3. Occurrence and spatial and seasonal variation of target organic pollutants according to 346 usage group

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



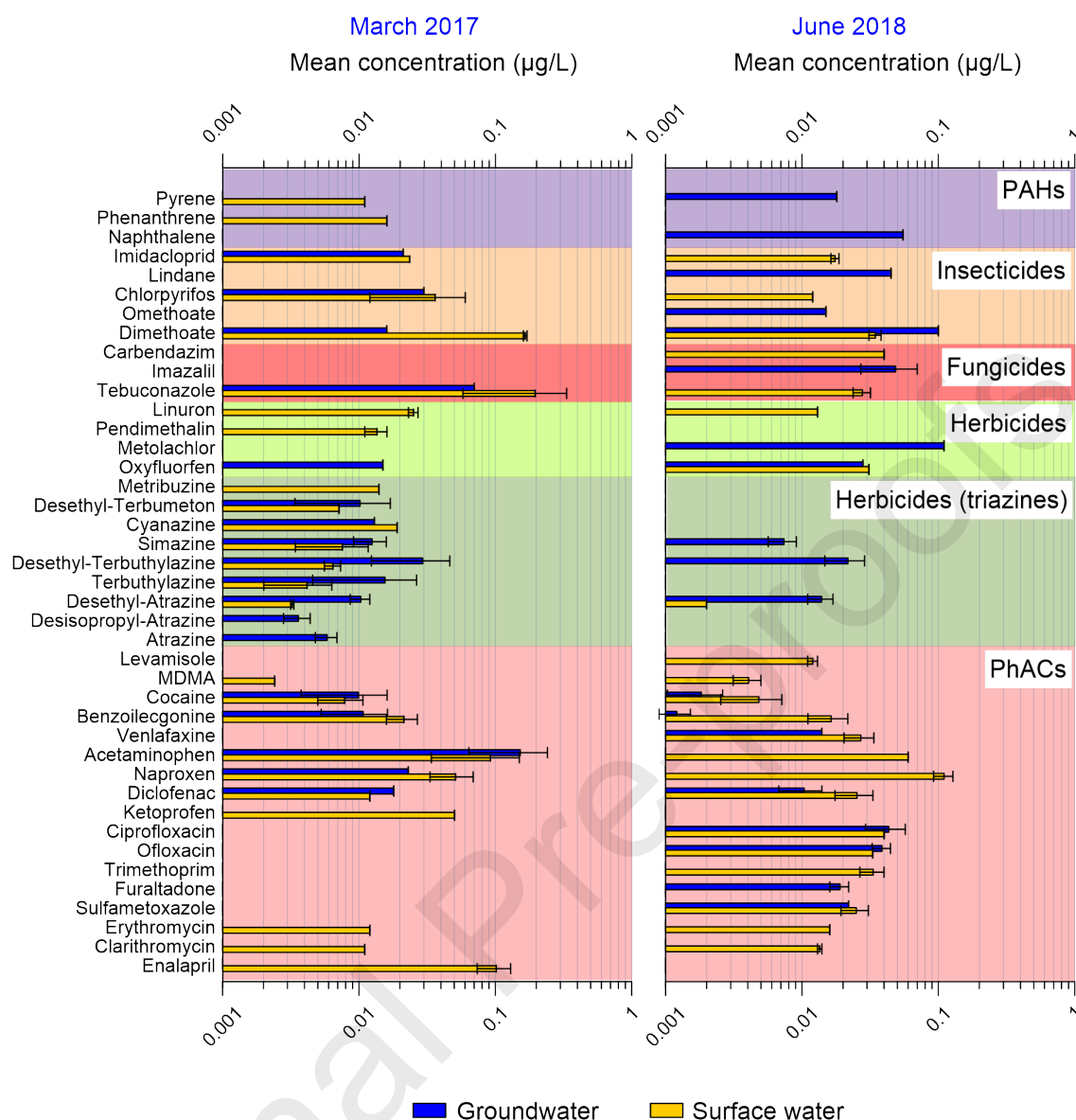
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Fig. 10. Frequency of detection (%) of organic contaminants in surface water and groundwater from the VG aquifer in the two monitoring campaigns (March 2017 and June 2018). Legend: PAHs: polycyclic aromatic hydrocarbons; PhACs: pharmaceutical active compounds.



358

359 **Fig. 11.** Average concentration ($\mu\text{g/L}$) and error bars of detected organic contaminants in surface water
 360 and groundwater from the VG aquifer in the two monitoring campaigns (March 2017 and June 2018).

361 Legend: PAHs: polycyclic aromatic hydrocarbons; PhACs: pharmaceutical active compounds.

362

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

367

368 As regards pesticides, 7 out of 16 were detected more often in groundwater in March
 369 2017; in June 2018, only 3 out of 14 were detected more frequently in groundwater. These are
 all triazines, which are herbicides. The rest include other herbicides, fungicides and insecticides.

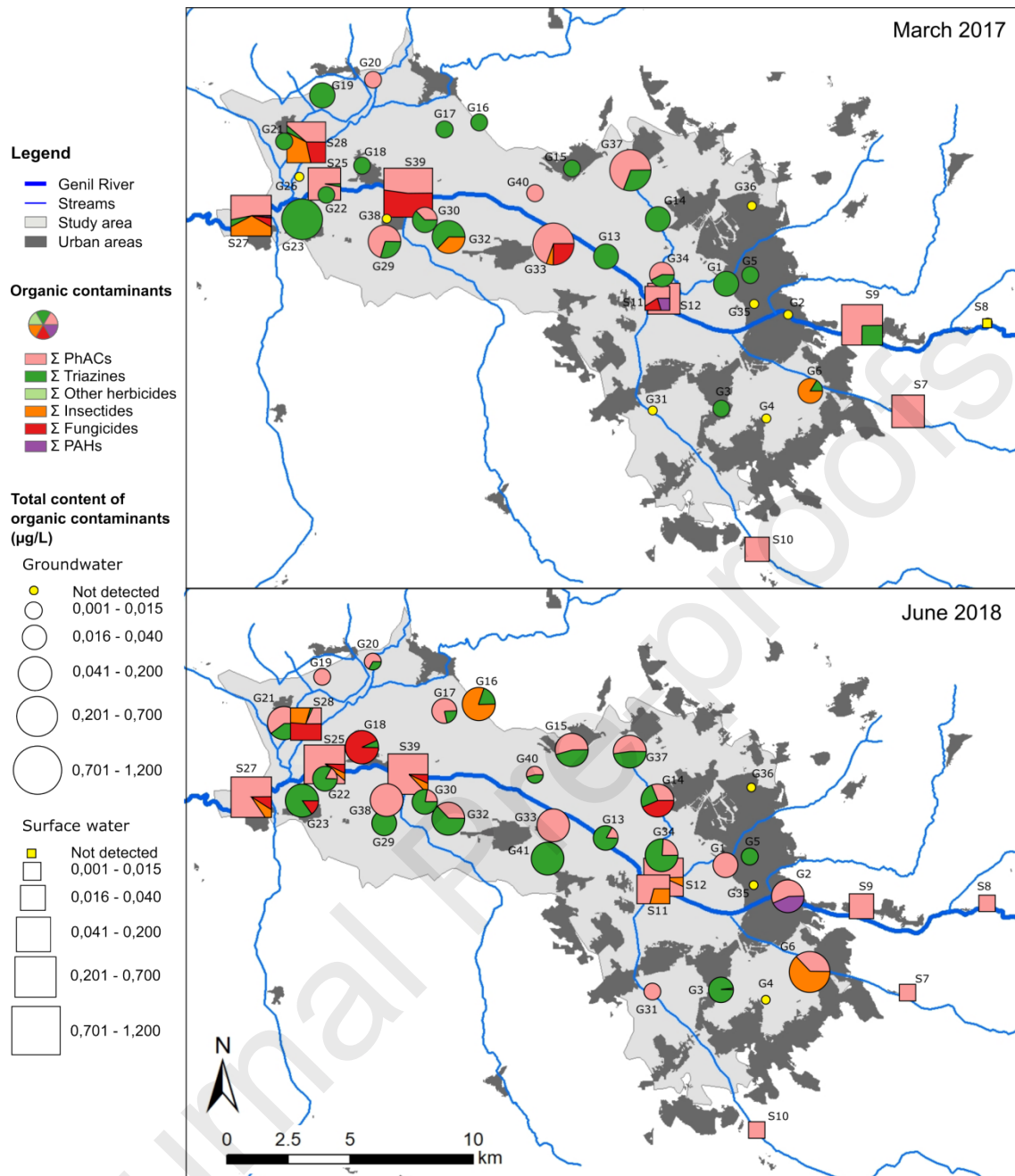
370 Herbicides are applied directly to the soil in agricultural lands as a diffuse source and they
371 would be expected to reach the water table through wash-off and release from the soil
372 granulates before reaching the streams. In contrast, fungicides and insecticides are generally
373 applied to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

385 Regarding all data, concentrations ranged from 0.0002 µg/L for cocaine in surface water
386 (June 2018) to a maximum of 0.6 µg/L of pesticide terbuconazole in surface water (March
387 2017). Minimum, maximum and mean values of organic contaminant concentrations are
388 available in Table S6 and S7. Priority substances naphthalene, atrazine, chlorpyrifos and
389 simazine were detected under the Environmental Quality Standards established for these
390 substances in surface waters (European Parliament and the Council of the European Union,
391 2013). Although lindane (γ isomer of hexachlorocyclohexane) was only detected in
392 groundwater, its concentration exceeded the limit set for surface waters in Directive 2013/39/UE
393 (> 0.04 µg/L). In the monitoring campaign carried out in March 2017, the limit set for individual
394 pesticides in groundwater (Directive 2006/118/EC; European Parliament and Council of the
395 European Union, 2006) is exceeded in sampling point G23 (0.24 µg/L of desethyl-terbutylazine).
396 In the June 2018 monitoring campaign, this limit was exceeded in sampling point G41 (0.11
397 µg/L of metolachlor).

398 The following contaminants detected in this study are included in the latest Watch List
399 (Decision (EU) 2020/1161; European Commission, 2020): pesticides imazalil and tebuconazole

400 and pharmaceuticals ciprofloxacin, sulfamethoxazole, trimethoprim, and venlafaxine.
401 Erythromycin and clarithromycin were the only detected pharmaceuticals that are included in
402 the first Voluntary Groundwater Watch List, although they were found only in surface water.
403 Therefore, none of the pollutants included in that list were detected in groundwater in this study.

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



411

412 **Fig. 12.** Pie charts of detected organic pollutants according to usage group in groundwater (circles) and
 413 surface water (squares) for both monitoring campaigns. Total pollutant concentration is indicated by size of
 414 circles and squares.

415

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

420

421 4.4. Selected pharmaceutical active compounds (PhACs)

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

425 Diclofenac was detected in one groundwater sample (0.018 µg/L) and in one surface
426 water sample (0.012 µg/L) collected on March 2017. In the June 2018 monitoring campaign its
427 frequency of occurrence increased substantially: it was then detected in 53% of groundwater
428 samples (0.010 ± 0.014 µg/L) and in all surface water samples (0.025 ± 0.024 µg/L). Diclofenac
429 is an anti-inflammatory agent and it was one of the most reported CECs in European
430 groundwater in recent years (Bunting *et al.*, 2021). In spite of its relatively high octanol-water
431 partition coefficient ($\log K_{ow} = 4.51$), diclofenac is an acidic compound with a $pK_{a,acid}$ value of
432 4.15, which means that only the ionized form (negatively charged) exists in solution with $pH \geq$
433 6.15 (Biel-Maeso *et al.*, 2017). pH field measurements ranged from 6.8 to 8.7 in this study. This
434 characteristic facilitates the mobility of the substance in the subsurface, since it avoids sorption
435 onto negatively charged surfaces of clays and organic matter (Schaffer and Licha, 2015).
436 Diclofenac can be quickly removed by biodegradation in agricultural soils (< 7 days), as
437 observed by Thelusmond and co-workers (2018).

438 Benzoylecgonine is the major metabolite of cocaine. It is formed by hydrolysis of cocaine
439 in the liver of cocaine users. These two substances showed a relatively high frequency of
440 detection in both campaigns. In March 2017, benzoylecgonine was detected in 90% of surface
441 water samples (with a mean concentration of 0.021 ± 0.016 µg/L) and in 13% of groundwater
442 samples (mean of 0.011 ± 0.01 µg/L); cocaine was found in 50% of surface water samples
443 (0.008 ± 0.006 µg/L) and in 16% of groundwater samples (0.010 ± 0.013 µg/L). An increase was
444 observed in June 2018: benzoylecgonine showed a frequency of detection of 37% in
445 groundwater (0.001 ± 0.001 µg/L) and still a 90% in surface water (0.016 ± 0.016 µg/L); cocaine
446 showed a frequency of detection of 70% in surface water (0.005 ± 0.006 µg/L) and 13% in
447 groundwater (0.002 ± 0.002 µg/L).

448 Benzoylecgonine can remain in the body of users longer and in larger quantities than
449 cocaine (Pal *et al.*, 2013) and, once in the environment, cocaine can be rapidly degraded,
450 mainly by hydrolysis, whereas benzoylecgonine can persist in the aquatic environment even

451 after 15 days from the time of discharge (McCall *et al.*, 2016), which can explain why it shows a
452 more widespread distribution than its parent compound. Benzoylecgonine contains both an
453 acidic and basic functional group, making it a zwitter ion (Skopp & Pöltsch, 1999; White &
454 Moore, 2018). Cocaine is a base with a $pK_{a,base} = 8.6$ (Kim *et al.*, 2019), which means that it can
455 be present partially as a cation under environmental pH conditions. Hence, the ionized form can
456 be more easily subjected to sorption processes, which would not be the case for the non-
457 ionized form. Both substances are rather hydrophilic because they have a relatively low $\log K_{ow}$
458 (2.3 and 1.3 for cocaine and benzoylecgonine, respectively; Skopp & Pöltsch, 1999), so they
459 are expected to sorb poorly onto solid particles and be present in the aqueous phase.

460 4.5. Selected pesticides

461 Triazines were the most ubiquitous group of pesticides (Fig. 10), especially in
462 groundwater, which is consistent with other European surveys (Loos *et al.*, 2010; Tasca *et al.*,
463 2018). Terbutylazine is one of the most widely used herbicides, mostly because of the ban on
464 the use of atrazine in Europe since 2004 (European Commission, 2004). However, both
465 substances are potentially used in the area in similar amounts, since metabolites desethyl-
466 terbutylazine and desethyl-atrazine were the most frequently found compounds within this
467 group, both reaching a frequency of detection of 47% in groundwater and 30% in surface water
468 in the March 2017 monitoring campaign. In June 2018, these two compounds, along with
469 simazine, were the only triazines detected and almost exclusively in groundwater: desethyl-
470 terbutylazine was found in 50% of groundwater samples; desethyl-atrazine was found in 53%
471 of groundwater samples and in 10% of surface water samples.

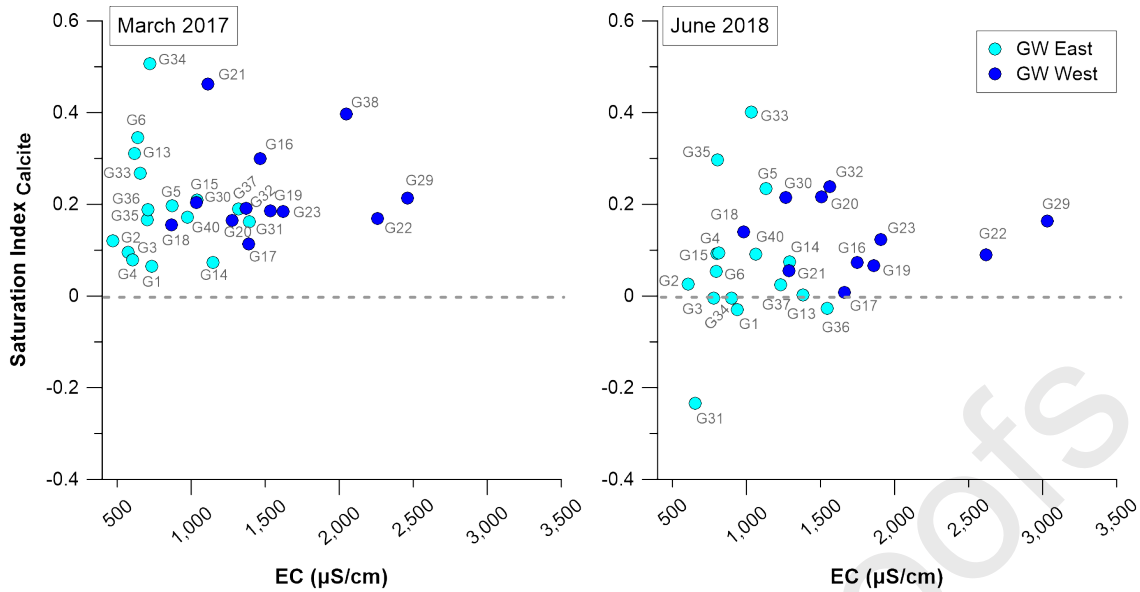
472 Terbutylazine is a very weak base ($pK_a = 2$), meaning that it is present as a non-ionized
473 molecule over almost the entire pH range (Tasca *et al.*, 2018) and its persistence in soils is
474 attributed to a strong adsorption capacity on humic substances (Navarro *et al.*, 2004). Its
475 metabolite, desethyl-terbutylazine, is more likely to pollute groundwater since it has a higher
476 water solubility and does not bind as strongly to organic matter as terbutylazine does (Tasca *et*
477 *al.*, 2018). Indeed, terbutylazine has a higher $\log K_{ow}$ (3.2; Tasca *et al.*, 2018) than desethyl-
478 terbutylazine (1.94; Ronka and Bodylska, 2021). Similarly, atrazine and desethyl-atrazine are
479 weak bases ($pK_a = 1.6$ and 1, respectively) and present a $\log k_{ow}$ of 2.61 and 1.51, respectively.
480 Therefore, the metabolite has a greater capacity to contaminate groundwater than the parent

481 compound (Aelion & Mathur, 2001). The weak base simazine might behave the same way as
482 atrazine since it has a pK_a value of 1.62 and a $\log K_{ow}$ value of 2.18 (Tomlin, 1997).

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

490 4.6. Assessment of the fate of selected organic pollutants in the VG aquifer

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



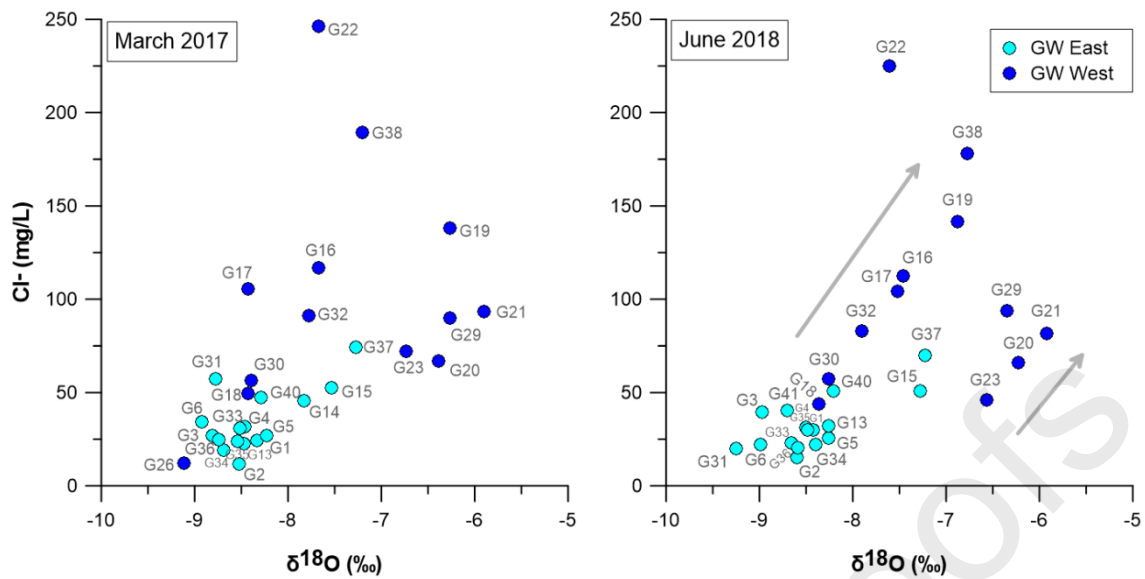
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509 **Fig. 13.** Calcite saturation index and electrical conductivity in groundwater from the eastern sector (sky
 510 blue) and from the western sector (navy blue) of the VG aquifer.

511

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

524

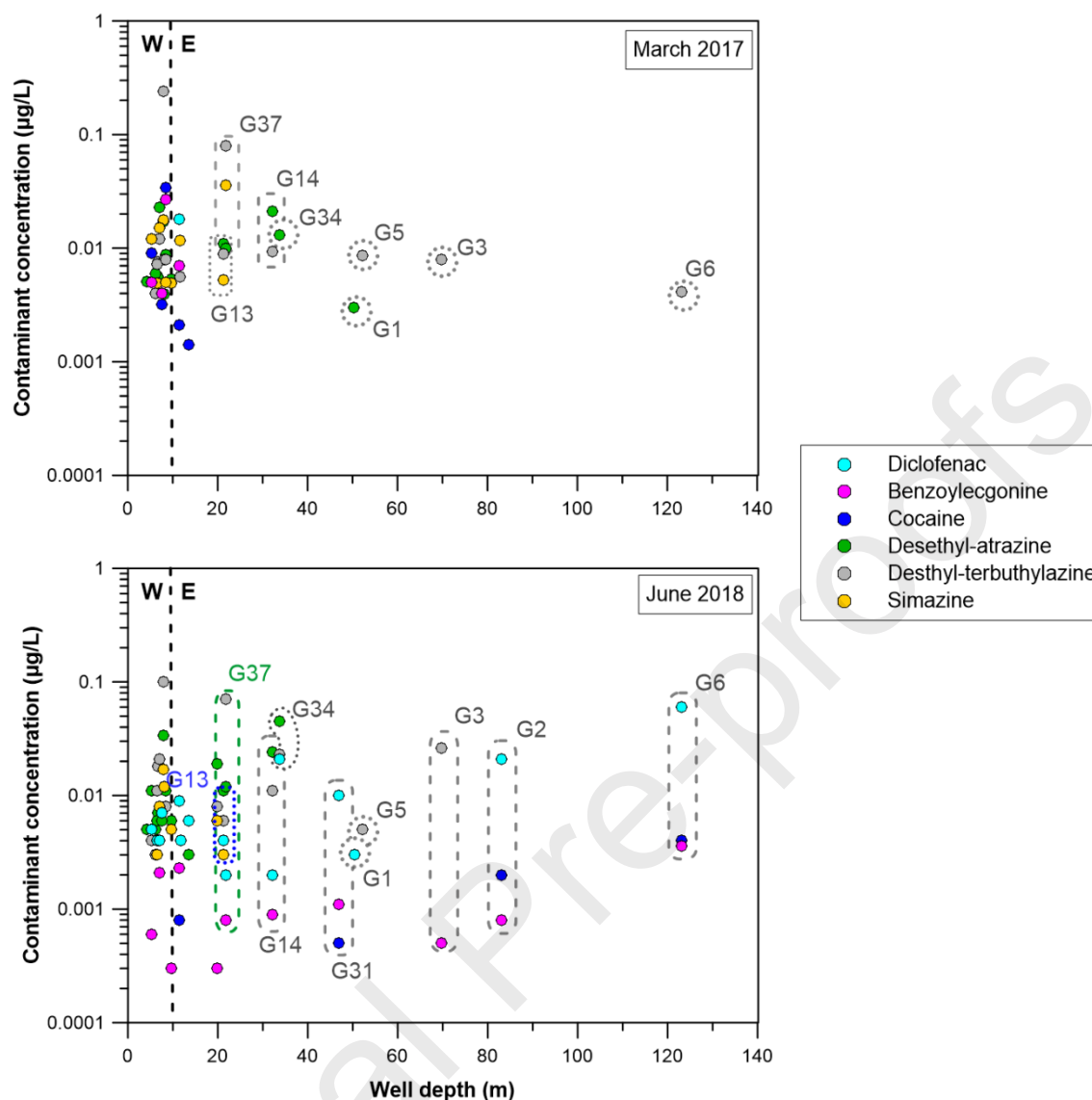


525

526 **Fig. 14.** Relationship between chloride (mg/L) and $\delta^{18}\text{O}$ (‰) in groundwater (GW) from the eastern sector
 527 (sky blue) and from the western sector (navy blue) of the VG aquifer.

528

529 Water transfer from the riverbeds and from irrigation to the aquifer may generate a
 530 widespread expansion of certain organic pollutants, especially PhACs. Fig. 15 shows the
 531 relationship between the presence and concentration of selected contaminants and the
 532 minimum well depth. Because, in all cases, wells are slotted all across the saturated zone, the
 533 well depth in Fig. 15 corresponds to the unsaturated zone thickness found at each well location.
 534 It can be observed that, in March 2017, most contaminants are detected in the shallowest wells,
 535 most of which are located in the western part of the aquifer (Fig. 3). In contrast, in the June
 536 2018 monitoring campaign, selected pharmaceuticals become almost ubiquitous throughout
 537 much of the aquifer. The occurrence of desethyl-atrazine, desethyl-terbutylazine and simazine
 538 between campaigns throughout the aquifer thickness does not change as significantly as that of
 539 pharmaceuticals.



540

541 **Fig. 15.** Relationship between detected organic contaminant concentration in groundwater ($\mu\text{g/L}$) and
 542 depth of monitored wells. Dashed line indicates the eastern-western sectors limit.

543

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

547 G6, G2 and G31 are located near the Monachil, Genil and Dílar Rivers, respectively (Fig.
 548 1), where the aquifer consists of fluvial gravels and sands and has the highest transmissivity
 549 values. The isotopic composition ($\delta^{18}\text{O}$) recorded in these wells is lighter in June, in line with the
 550 oxygen-18 depletion of the aforementioned rivers (Fig. 8). S_{Icalcite} measured in these
 551 groundwater samples is lower (Fig. 13), suggesting recharge from surface fresh water.
 552 Therefore, in the case of these wells, recharging streams can be the path through which organic

553 contaminants enter the groundwater. The Monachil and Dílar Rivers receive untreated
554 wastewater discharges right before they enter the Granada plain, according to the basin
555 authority (Fig. 4); two WWTP discharge into the Genil River before water enters the plain (Fig.
556 S1). In June, surface water samples S7 (Monachil River), S8, S9 (Genil River) and S10 (Dílar
557 River) showed detectable concentrations of diclofenac (from values below limit of quantification
558 to 0.015 µg/L); S7, S8 and S9 showed detectable contents of benzoylecgonine (from values
559 below limit of quantification to 0.005 µg/L) and S7 and S9 showed detectable contents of
560 cocaine (below limit of quantification).

561 WWTPs in the Granada area include secondary treatment, which can be very effective in
562 eliminating cocaine and benzoylecgonine, with removal rates above 88% (Huerta-Fontela *et al.*,
563 2008), but are extremely unsuccessful in removing diclofenac (Kasprzyk-Hordern *et al.*, 2009),
564 which requires tertiary treatment (Alessandretti *et al.*, 2021).

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

580 Sampling point G36 did not show any detectable content of organic pollutants in any
581 monitoring campaign (Fig. 12), and sampling point G5 showed a relatively low and similar
582 concentration of triazines in both campaigns (Fig 15), which are less mobile than the

583 pharmaceuticals. This general absence of organic pollutants at these two points can be
584 attributed to the fact that they are located in the northeastern part of the aquifer, where the
585 hydraulic gradient is steeper (Fig. 3) due to a higher clay content (Mateos *et al.*, 2017). In
586 contrast, diclofenac was detected in June in G1, which is closer to a stream (Beiro River) in a
587 zone where the aquifer materials become coarser and the hydraulic gradient decreases.

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

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

603 **5. Conclusions**

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

609 A simple representation of the spatial distribution of the organic contaminants in the study
610 area (Fig. 12) is not easy to interpret. The wide variety of factors influencing the occurrence of
611 these pollutants makes spatial and seasonal analysis a challenging task. Physico-chemical and
612 hydrochemical parameters along with environmental stable isotopes have been used to define

613 the hydro(geo)logical context of the study area during the monitoring campaigns. This has
614 contributed to the understanding of the spatial and seasonal distribution of the contaminants.

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

637 Finally, the importance of the anthropogenic factor cannot be ignored, as evidenced by
638 the opposite seasonal tendency regarding frequency of detection of pharmaceuticals and
639 herbicides. Typical pesticide application periods can explain the appearance of herbicides in
640 March and their frequency detection decrease in June. The increase of urban water demand
641 (potentially due to growth of tourism in summer) can also explain a higher frequency of
642 detection of pharmaceuticals and drugs of abuse in June in both surface water and

643 groundwater. Intensification of irrigation should also be considered as a potential path of entry
644 of urban organic contaminants. Treated and untreated urban wastewater is released to streams,
645 from which water is diverted for irrigation, and also discharged directly into irrigation channels
646 and ditches.

647 The hydrodynamic context in the study area drives the greatest changes between
648 seasons in the southeastern part of the aquifer, where transmissivity values are greater. Further
649 research will focus on these zones and will require conducting more frequent monitoring work
650 over time to better characterize this phenomenon. Research funds will be more efficiently spent
651 by monitoring just the most frequent compounds detected in this work.

652

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660

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927 **Highlights**

- 928 • Pharmaceuticals and pesticides assessed in surface water and groundwater.
929 • Pollutants occurrence in water resources mention the way they are released.
930 • Aquifer recharge from streams contributes to the spread of pharmaceuticals.
931 • Unsaturated zone protective power is observed although it is not always impassable.

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