



Research article

Study of the presence and environmental risk of organic contaminants policed by the European Union and other organic compounds in the water resources of a region overlapping protected areas: The Guadiaro River basin (southern Spain)

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ABSTRACT

The study presented here is a first qualitative assessment of the occurrence of organic contaminants contemplated and not yet contemplated in European Union environmental legislation in water resources in the little anthropized Guadiaro River basin (70% of its area is covered by natural vegetation), in southern Spain. Water samples were collected from four carbonate aquifers, two detrital aquifers and four surface water courses and were analyzed for (i) 171 organic contaminants, (ii) major ions and (iii) stable isotopes ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta^2\text{H}_{\text{H}_2\text{O}}$, $\delta^{13}\text{C}_{\text{DIC}}$). An environmental risk assessment was conducted through calculation of risk quotients comparing measured concentrations with ecotoxicological data found in the literature. Twenty-five organic contaminants were detected, at least once, including pesticides, pharmaceuticals, drugs of abuse and polycyclic aromatic hydrocarbons (PAHs). Cocaine and its main metabolite were detected in 85% and 95% of water samples, respectively (0.001–0.18 $\mu\text{g}/\text{L}$ and 0.004–0.6 $\mu\text{g}/\text{L}$, respectively). Pyrene (PAH) was found in all water samples (0.001–0.015 $\mu\text{g}/\text{L}$) and forest fires were pointed out as a potential diffuse source. Relationship between rivers and aquifers is reflected by the distribution of organic contaminants, essentially the drugs of abuse. Concentration of contaminants were generally higher in groundwater samples, especially from detrital aquifers, potentially due to an accumulation process promoted by irrigation-return flows and by its slow dynamic compared to that of karstic systems. Pyrene concentration was also higher in some springs from karstic aquifers. Hence, calculated risk quotients were in general higher in groundwater, meaning that the threat to surface aquatic systems can grow as aquifers increase their influence on the water courses as the dry season progresses. The relationship between $\delta^{13}\text{C}_{\text{DIC}}$ and most organic contaminants (especially pyrene) reveal the role of the soil as storage media.

1. Introduction

Daily domestic actions along with industrial and agricultural activities entail an input of a broad spectrum of pollutants into the environment. Among them, persistent organic pollutants (POPs) have been of concern for at least two decades due to their capacity to bioaccumulate, their toxicological risk to living beings (Nadal et al., 2015), their significant resistance to degradation and the possibility of being transported over long distances through the atmosphere and

hydrosphere (Wania and Mackay, 1996; Ockenden et al., 2003). Historically, to tackle this issue, lists of “priority pollutants” have been drawn up at an international scale, aiming to ban/restrict its use and release (e.g., Aarhus protocol in 1998, Stockholm Convention in 2001; Nadal et al., 2015). The type of organic contaminants (OCs) found in these lists and currently subjected to environmental regulations includes pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), among others. Contaminants of Emerging Concern (CECs), more recently considered a potential threat to the environment

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and to human health (Lapworth et al., 2012), include pharmaceuticals and drugs of abuse, among others, and are being detected in water all over the world (Bunting et al., 2021; Wilkinson et al., 2022; Reberski et al., 2022). However, their persistence in the aquatic environment is largely attributed to its continuous release mainly through wastewater discharges (Daughton, 2004). In the European Union, four “Watch lists” including emerging pollutants have been published since 2015 to possibly consider their official recognition as priority pollutants in the future (European Commission, 2022a). The Spanish national legislation on water quality included a few emerging pollutants to be monitored in water for urban supply (BOE, 2023, Real Decreto 3/23). On October 26th of 2022, the EU Commission published a proposal for amending the Water Framework Directive, the Groundwater Directive, and the Directive on Environmental Quality Standards. In this document, some emerging contaminants (e.g., some pharmaceuticals) have been included to the list of priority substances and to the groundwater quality standards (European Commission, 2022b, 2022c).

Most research about CECs in the environment have focused on surface water and wastewater (Lapworth et al., 2019). Groundwater is a key element to study due to direct pollution sources (e.g., septic tanks, landfill leachates, fertilization with manure and sewage sludge; Biel-Maeso et al., 2019; Watanabe et al., 2010) and their interconnection to surface water bodies, which can affect the distribution of OCs including PAHs, pesticides and CECs (Li et al., 2017; Llamas et al., 2021, 2022). However, assessing their spatial distribution is still challenging due to the influence of many factors such as different physico-chemical behaviors of the pollutants, heterogeneous content of pollution sources and their uneven spatial distribution and the diversity of the hydrogeological conditions (Boy-Roura et al., 2018).

A relatively strong presence of OCs (including CECs) have been reported in surface water and groundwater of heavily anthropized areas in southern Spain linked to a great lack of wastewater treatments and an intense use of water resources for agricultural activities and urban supply (Luque-Espinar et al., 2015; Luque-Espinar and Chica-Olmo, 2020; Llamas-Dios et al., 2021; Llamas et al., 2022). The study site of this research is the Mediterranean basin of the Guadiaro River, the largest river flowing through the province of Malaga (southern Spain). Unlike the other studied areas in the region, the Guadiaro River basin present few anthropogenic pressures and more than half of the basin surface (56%) belongs to the European Commission’s Natura 2000 Network (Herrera et al., 2019). However, the lack of wastewater treatment for urban wastewater is common throughout the basin (Junta de Andalucía, 2010; Junta de Andalucía, 2021a), which raises the concern about the potential presence of contaminants resulting from domestic activities in the watercourses and the related aquifers.

The hydrogeological and environmental characteristics of the main carbonate aquifer systems within the Guadiaro River basin have been described (e.g., Jiménez-Gavilán et al., 2003; Andreo et al., 2005; Andreo et al., 2006; Jiménez-Gavilán, 2011; Barberá-Fornell, 2014; Barberá et al., 2014; De la Torre et al., 2020). The scientific information available about the detrital aquifers of the basin is less abundant (e.g., Jiménez-Gavilán and Morales-García, 2007; Morales-García, 2007). To date, no aquifer within the Guadiaro River basin have been monitored CECs, except for the study that is presented here.

As mentioned, OCs mostly reach surface waters through the discharge of treated and untreated wastewater (Carballa et al., 2004; Biel-Maeso et al., 2018). Once this happens, aquatic organisms are exposed to a wide range of possible adverse effects such as genotoxicity, alteration of sex ratios and development, behaviour changes, decrease of motility and metabolism and increase in the mortality of the organisms (in some cases these effects are caused by endocrine disruption mechanisms; López-Pacheco et al., 2019).

The identification of the factors influencing the occurrence of OCs in the aquatic environment, and thus the exposure, is necessary to estimate potential risks. Hence, the first objective of this study is to investigate the spatial distribution of a wide array of OCs (including CECs) in

groundwater and surface water of the Guadiaro River basin. The analytical method applied includes 171 target compounds. Thus, a general overview of the situation regarding water pollution by OCs is yielded. To understand the presence of the OCs throughout the basin, we use previous hydrogeological knowledge of the monitored aquifers and hydrochemical and isotopic tools. The second objective is to evaluate the environmental risk of the detected compounds in streams based on ecotoxicological data of aquatic organisms of three trophic levels (algae, invertebrates and fish) according to the Technical Guidance Document of Risk Assessment of the European Union (ECB, 2003). The monitored aquifers are closely linked to the studied water courses through springs or lateral groundwater flow. Therefore, groundwater samples have been also included in the environmental risk assessment.

2. Site description

The Guadiaro River basin (1505 km²) is located in the south of the Iberian Peninsula, in the provinces of Cádiz and Málaga (Spain; Fig. 1). The Guadiaro River (82 km long) starts in the middle of the Ronda depression, after the confluence of the Guadalcoacán and Guadalevín Rivers, and it flows into the Mediterranean Sea, next to San Roque town (Fig. 1). In the lower part of the basin, the Guadiaro River is fed by its two main tributaries: the Genal and Hozgarganta Rivers. The elevation ranges from approximately 1700 m above sea level (m a.s.l) in the mountainous area in the northeastern part of the basin to the coast, in the south of the basin (IAECA, 2019). In the mountainous areas located in the upper part of the basin, rainfall and temperature annual mean values are 900–1000 mm and 16–17 °C, respectively. The lower part of the basin is more influenced by the sea and its rainfall and temperature annual mean values are 800–900 mm and 17–18 °C, respectively (Morales-García, 2007).

The rocks within the basin belong to the three main tectonic bodies of the Betic Cordillera (the External Zone, the Flysch Complex and the Internal Zone; Fig. 1) and to post-orogenic formations (Serrano-Lozano and Guerra-Merchán, 2005). The Internal Zone is on the western part of the basin and comprises Triassic to Early Miocene carbonate formations, metamorphic rocks of Paleozoic age and igneous rocks. In the northern half of the basin, the External Zone presents outcrops of Late Triassic clays, dolostones, sandstones and evaporite rocks (mainly gypsum); Jurassic limestones and dolostones; and Early-Tertiary loamy-limestones and marls. The Flysch complex broadly extends over the southern part of the basin and partly over the northern part. It is mostly formed by Cretaceous-Tertiary clays and sandstones (Jiménez-Gavilán and Morales-García, 2007; Roldán et al., 2021). Post-orogenic materials overlay the latter formation in the south of the river basin: Pliocene deposits (mainly sands) and Quaternary alluvial sediments. In the most north part of the hydrographic basin, the Ronda’s Neogene post-orogenic basin is composed of calcarenites, conglomerates and marls of Miocene age; and some Quaternary fluvial deposits can be found, which are related to the water courses in the area (Jiménez-Gavilán and Morales-García, 2007).

Groundwater samples are from the main aquifers in the river basin (Table 1), which are linked to the main water courses. Sampling points G3 and G13 are wells pumping water from the deposits of the Ronda’s Neogene basin (Fig. 1), which form a porous unconfined aquifer that mostly lays over clays from the Flysch Complex. However, an elevation of the Triassic formation (clays and evaporite rocks) beneath the Neogene materials in the western part of the aquifer sets a hydrogeology limit, coinciding with the hydrographic limit of the basin (Fig. 1). The groundwater recharge in this aquifer takes place mainly through infiltration of rainwater but also through underground flows coming from the surrounding Jurassic (External Zone) and Triassic carbonate materials (Internal Zone; Jiménez-Gavilán and Morales-García, 2007), while an important discharge rate feeds the Guadalcoacán River (sampling point S4; Fig. 1), which also receives resources in this area from small tributaries formed by runoff (Jiménez-Gavilán and Morales-García,

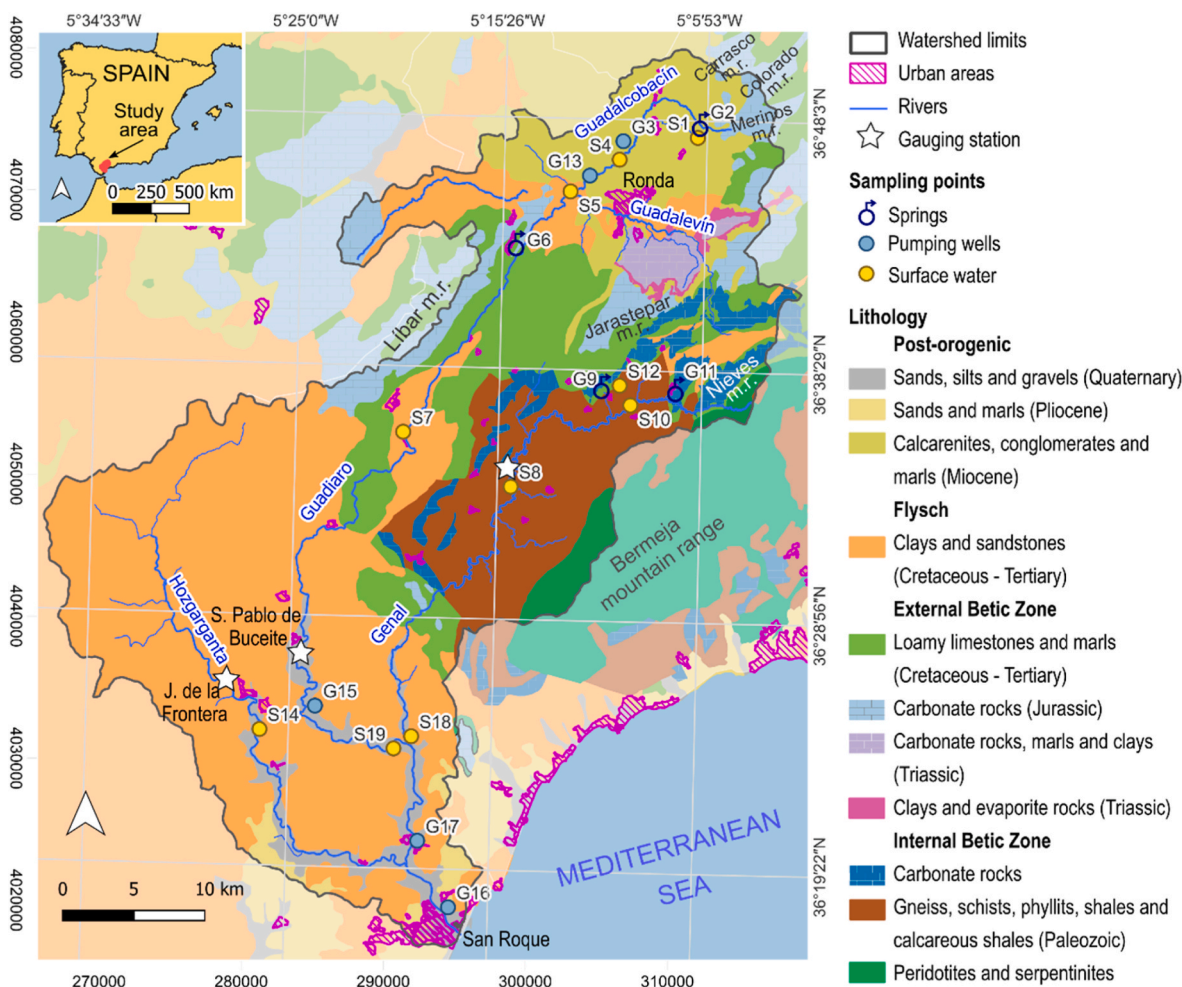


Fig. 1. Location and lithological map of the Guadiaro River basin (modified from IAECA, 2019; Roldán et al., 2021) and location of sampling points of groundwater (GX; springs and pumping wells) and surface water (SX). Note: “m.r.” means mountain range.

Table 1
Groundwater sampling points and the aquifer formations they belong to.

Aquifer formation	Type of aquifer	Sampling points
Deposits of the Ronda’s Neogene basin	Porous unconfined	G3 (pumping well) G13 (pumping well)
Merinos-Colorado-Carrasco system	Karstic carbonate	G2 (Ventilla spring)
Libar m.r.	Karstic carbonate	G6 (Benaoján spring)
Las Nieves m.r.	Karstic carbonate	G11 (Igualeja spring)
Jarastepar m.r.	Karstic carbonate	G9 (La Zúa spring)
Genil-Genal-Hozgarganta aluvial deposits	Porous unconfined	G15 (pumping well) G16 (pumping well) G17 (pumping well)

2007). The Merinos-Colorado-Carrasco aquifer system is formed largely by karstified limestones and its groundwater transfer towards the porous Ronda’s aquifer becomes visible at the Ventilla spring (sampling point G2; Barberá et al., 2014). Jurassic carbonate rocks make up a karst aquifer in Lfbar mountain range (Fig. 1), whose springs on its southern and eastern border discharge towards the Guadiaro River, e.g., Benaoján spring (G6). The origin of the Genal River is the Igualeja spring (G11), which drains a karst aquifer formed by carbonate outcrops from the Internal Zone in Las Nieves mountain range and surrounding areas (Andreo et al., 2005). Jurassic and Triassic rocks from Jarastepar mountain range and surrounding areas are hydrogeologically connected (De la Torre et al., 2020). Its springs (e.g., G9, La Zúa spring) to a large

extend discharge into the upper stretch of the Genal River. Sampling points G15, G16 and G17 (Fig. 1) are pumping wells drilled in the aquifer formed by the Quaternary alluvial deposits of the three main rivers in the basin: Genil, Genal and Hozgarganta rivers (Fig. 1). The Pliocene sedimentary materials in the lower part of the basin form an aquifer that is hydrogeologically connected to the Quaternary aquifer by the mouth of the Guadiaro River. Water recharge in both aquifers take place through infiltration of rainfall on outcropping materials and through infiltration of surface runoff coming from adjacent impervious materials at their borders. Additional water sources in the Quaternary aquifer are irrigation return flows and surface water infiltration from the three main rivers (Morales-García, 2007).

2.1. Pressures

The Guadiaro River basin is not considered to be heavily modified as roughly 30% of its area is cultivated (mainly in the Ronda depression, along the river valleys and on the alluvial Quaternary deposits in the south of the basin; Fig. 2a) and almost 40% has been given a regional or national protection status (i.e., Los Alcornocales and Sierra de Grazalema Natural Parks and Sierra de las Nieves National Park; IAECA, 2019). Most of the population is in Ronda town (Fig. 1; >30,000 inhabitants) and the rest of the urban centers are generally small (<2000 inhabitants). Treated and untreated urban wastewater is discharged into rivers and streams within the basin (Junta de Andalucía, 2010). The location and magnitude of urban wastewater discharges acknowledged by the basin authority is shown in Fig. 2b. The greatest volume comes

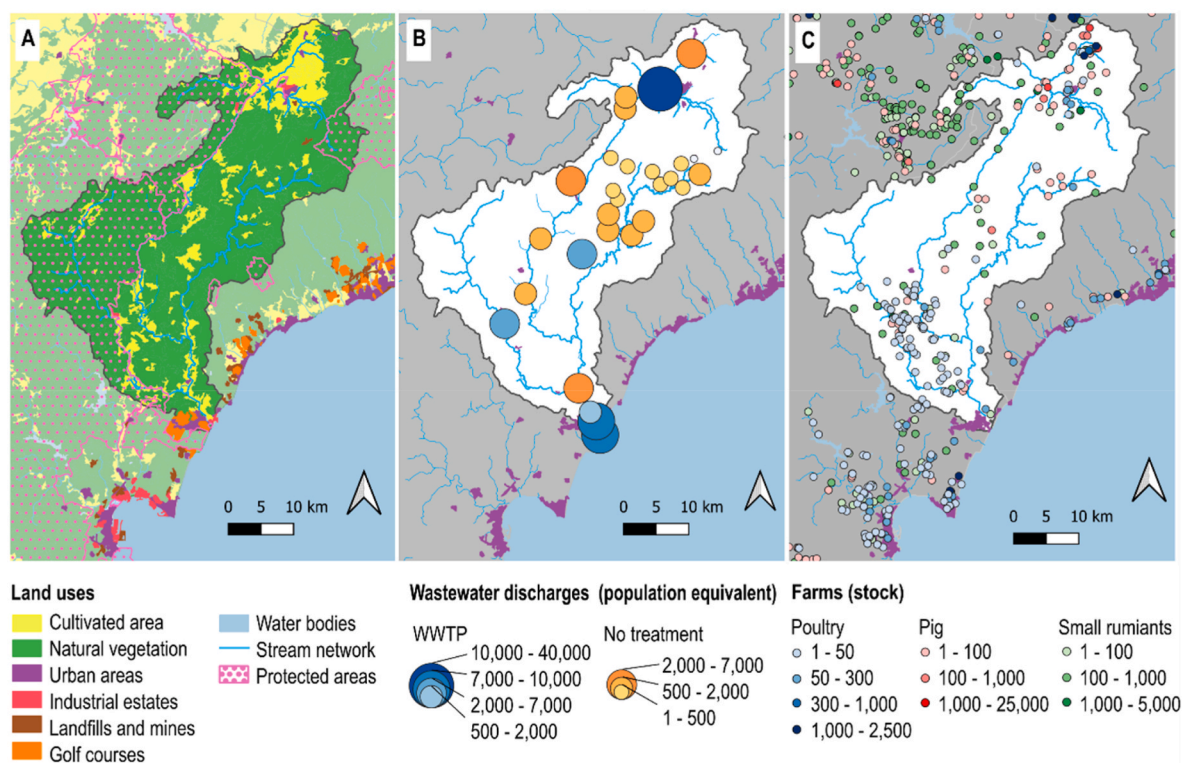


Fig. 2. (A) Land use (IAECA, 2019); (B) treated and untreated urban wastewater discharges and (C) livestock production sites in the Guadiaro River basin (Junta de Andalucía, 2010). Note: WWTP means wastewater treatment plant.

from the Ronda's wastewater treatment plant (WWTP). Purification processes in the WWTP consist of preliminary treatment, a primary sedimentation process, secondary biological treatment and secondary sedimentation. Most important livestock production sites (with higher number of animals) are in the upper part of the basin, in the Ronda depression (Fig. 2c). The river flow in the middle and low stretch of the Guadiaro River and in the low stretch of the Genal River (before the confluence with the Guadiaro River) diminishes greatly during the dry season because of water extractions mostly for irrigation (Junta de Andalucía, 2010; Junta de Andalucía, 2021a). Events of unusually high fish mortality have been detected in the middle reach of the Guadiaro River attributed to wastewater dumping and rivers flow rate reduction mostly in the summer season (Junta de Andalucía, 2010).

3. Materials and methods

3.1. Sampling campaign

The sampling campaign took place at the end of March 2017 and consisted of the collection of 10 surface water samples and 9 groundwater samples along the Guadiaro River basin (Fig. 1). Physico-chemical parameters (pH, temperature, electrical conductivity, redox potential and dissolved oxygen) were measured in-situ using a portable multi-parametric probe (Hach-Lange HQ40d; USA). Water samples were analyzed for (i) 171 organic pollutants (Table S1), (ii) major ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^- , NO_3^-) and (iii) isotopes from the water molecule ($\delta^{18}\text{O}$, $\delta^2\text{H}$) and from dissolved inorganic carbon ($\delta^{13}\text{C}$).

For hydrochemical (major and minor ions) and isotopic analysis, samples were stored in sterile and sealed 120 mL high-density polyethylene (HDPE) bottles with inverted cone caps. Samples collected for analysis of organic contaminants were stored in sterile 1 L amber glass bottles with Teflon caps to avoid sorption. All containers were pre-rinsed with the samples' own water, carried in a portable cool box ($<4^\circ\text{C}$) and sent out for analysis within 24 h. Sampling points G2, G6, G9 and G11

are springs, whereas the rest of the groundwater sampling points (G3, G13, G15, G16 and G17) are pumping wells (Fig. 1). In the latter case, samples were taken after continuous pumping.

3.2. Analytical methods

Hydrochemical and isotopic analyses were carried out in the laboratory of the Center of Hydrogeology of the University of Malaga (CEHIUMA). A Metrohm 881 Compact IC Pro HPLC system was used for determination of major and minor ions. A Picarro Water Isotope Analyzer L2120i (laser spectroscopy) was used for determination of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (‰; Vienna Standard Mean Oceanic Water). $\delta^{13}\text{C}$ from dissolved inorganic carbon (‰; Vienna Pee Dee Belemnite) was determined in a Picarro Carbon Isotope Analyzer G1111i-CRDS.

Water samples were analyzed for 171 organic pollutants (Table S1) in the laboratory of the company IPROMA, in Castellón (Spain). The occurrence of Pharmaceutical active compounds (PhACs), abuse drugs and polar pesticides and metabolites was analyzed by online 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 priority substances (PAHs, PCBs, organochlorine, organophosphorus pesticides, triazines and brominated diphenyl ethers) were analyzed by stir bar sorptive extraction (SBSE) followed by gas chromatography coupled to mass spectrometry (GC-MS; León et al., 2003; 2006). A list of analyzed organic pollutants and more information about the analytical methods applied for determination of organic compounds is available in Supplementary Material.

3.3. Principal Component Analysis (PCA)

A Principal Component Analysis (PCA) was computed to explore relationships between variables and to determine driving background processes (Kovács et al., 2012). PCA reduces the dimensionality of big datasets by creating new uncorrelated components or Principal

Components (PCs) from the original variables (Liu et al., 2017). The correlation coefficients between the original variables and the PCs are the factor loadings, which reflect how much weight a given variable has in each PC (Kovács et al., 2012). For interpretation, PCA results were represented in a loading plot and a PCA score plot. PC scores are the transformed variable value corresponding to each data point (in this case, water samples; Liu et al., 2017). The PCA was performed using the ‘stats’ package in the R software (R Core Team, 2021).

3.4. Environmental risk assessment

For the environmental risk assessment, risk quotients (RQ) were calculated for organic contaminants detected in water samples according to the Technical Guidance Document of Risk Assessment of the European Union (ECB, 2003). Briefly, RQs were determined by comparing the measured environmental concentration (MEC) of a certain compound with its PNEC (Predicted No Effect Concentration; Eq (1)). PNEC is estimated using the lowest ecotoxicological parameter available (i.e., median Effect Concentration [EC₅₀], median Lethal effect Concentration [LC₅₀], No Observed Effect Concentration [NOEC]), presuming that the ecosystem sensitivity depends on the most sensitive species, and an assessment factor (AF; Eq. (2)). Ecotoxicological data of organic contaminants towards aquatic organisms representing three different trophic levels (i.e., algae, invertebrates and fish) was gathered from the

literature (Table S2). An assessment factor is used to consider the uncertainty in extrapolating from laboratory toxicity test data for a limited number of species to the real environment (ECB, 2003). When only short-term toxicity data (EC₅₀ or LC₅₀) was available, regardless of whether or not the endpoints are available for more than one species, an AF of 1000 was applied; if one long-term toxicity data (NOEC) was available, an AF of 100 was used; if two NOECs for species representing two trophic levels were available, an AF of 50 was applied; and if NOECs from at least three species from three trophic levels were available, an AF of 10 was applied (ECB, 2003).

$$RQ = \frac{MEC}{PNEC} \tag{1}$$

$$PNEC = \frac{\text{lowest endpoint available (EC}_{50}, LC_{50} \text{ or NOEC)}}{AF} \tag{2}$$

4. Results

4.1. Hydrochemistry and isotopes

The hydrochemistry of water samples is shown in Fig. 3. Generally, the water quality is high as the electrical conductivity (EC) values ranged from 261 μS/cm (Benaoján spring, G6) to 1302 μS/cm (La Zúa spring, G9) and most water samples presented bicarbonate-calcium

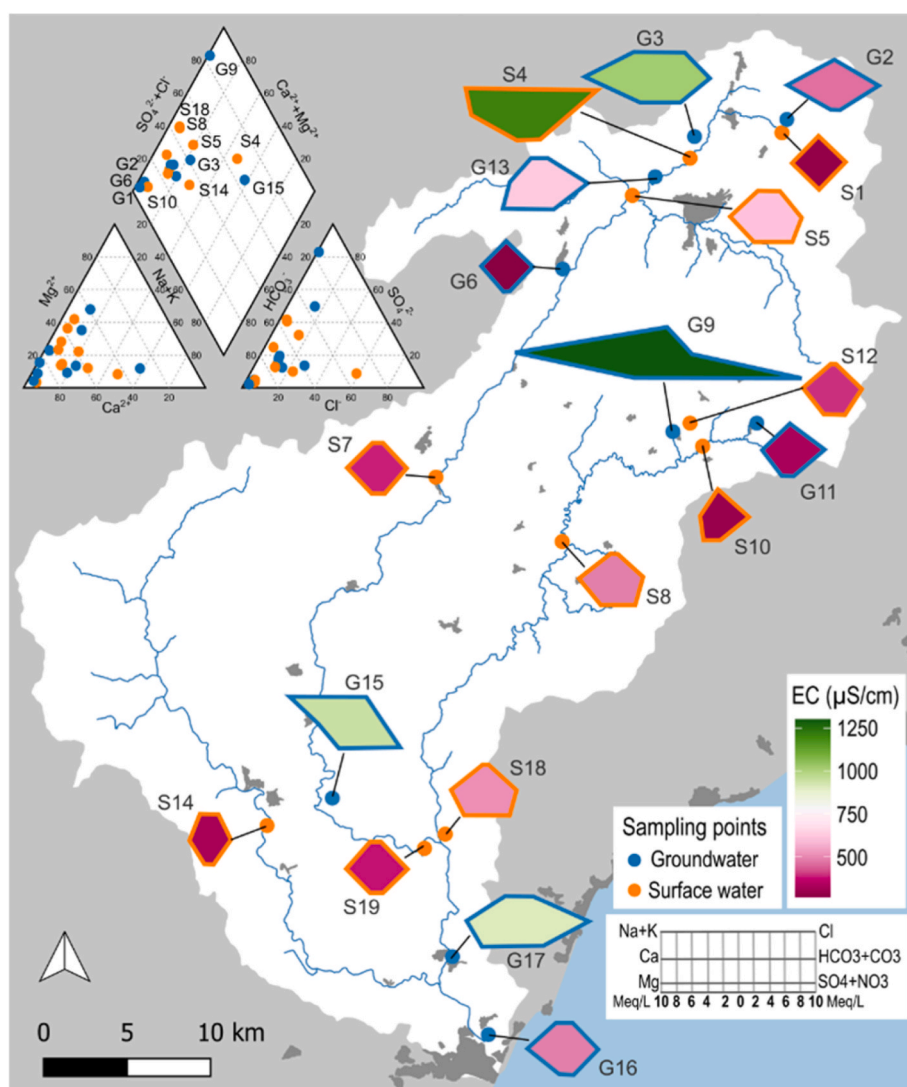


Fig. 3. Stiff and piper diagrams of water samples. Electrical conductivity (EC) is indicated by the fill color of stiff diagrams.

facies, except for S4, G9 and G15: these showed sodium-chloride, calcium-sulphate and sodium-sulphate facies, respectively. Nitrate concentration only surpassed the quality threshold value (50 mg/L; European Parliament and the Council of the European Union, 2006) in point G3 (63.7 mg/L) and presented an overall average value of 11.6 mg/L. Isotopic values ranged from -41.9‰ to -26.0‰ and from -7.2‰ to -4.8‰ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively. $\delta^{13}\text{C}$ values ranged from -15.5‰ to -7.9‰ . Monitored data is available in Supplementary Material (Table S4).

4.2. Organic contaminants

In total, 25 out of 171 target OCs were detected, at least once: three polycyclic aromatic hydrocarbons (PAHs), 11 pesticides of different kind (three fungicides: imazalil, thiabendazole and carbendazim; four herbicides: linuron, simazine, desethyl-terbutylazine, diuron and oxyfluorfen; and three insecticides: dimethoate, imidacloprid and chlorpyrifos), one drug of abuse and its metabolite (cocaine and benzoylecgonine), and nine PhACs (Fig. 4a).

Fig. 4 shows the frequency of detection and concentration of all detected OCs and their spatial distribution. Concentrations of OCs ranged from a minimum value of 0.001 $\mu\text{g/L}$ of pyrene in surface water to a maximum value of 0.6 $\mu\text{g/L}$ of benzoylecgonine in groundwater (Table S3). Pyrene, cocaine and benzoylecgonine were detected in more than 90% of water samples. Imidacloprid was found in more than 50% of water samples and the rest of compounds were detected in less than 50% of samples. Seventeen compounds were detected only in one sample.

No pesticide was detected at a concentration higher than the European limit (0.1 $\mu\text{g/L}$; Fig. 4a) set for these compounds in groundwater (Directive, 2006/118/EC; European Parliament and the Council of the European Union, 2006). The maximum concentration of total pesticides

was detected in groundwater sample G16 (0.12 $\mu\text{g/L}$), so the limit set for total sum of pesticides was not surpassed either (0.5 $\mu\text{g/L}$; European Parliament and the Council of the European Union, 2006). The priority substances (Directive, 2013/39/EU) detected in the monitored waters (chlorpyrifos, diuron and simazine) did not surpass the threshold value set for these compounds in surface waters (European Parliament and the Council of the European Union, 2013). The concentration of the antibiotic sulfamethoxazole in G16 was 0.05 $\mu\text{g/L}$, so it surpassed the quality standard of this substance (i.e., 0.01 $\mu\text{g/L}$) for groundwater indicated in the recent proposal of amendment of the European Commission for the Water Framework Directive, Groundwater Directive and the Directive on Environmental Quality Standards (European Commission, 2022c).

Fig. 4b shows the spatial distribution of the groups of OCs. Pyrene and imidacloprid have been represented with their own color since they showed a high frequency of detection. All water samples showed some content of OCs. Sampling point G15 presented the highest content (0.99 $\mu\text{g/L}$ as total concentration of all OCs detected in this sample), followed by sampling point S5 (0.81 $\mu\text{g/L}$). The sampling points showing the lowest content in OCs are G9 and S8, both with roughly 0.007 $\mu\text{g/L}$.

4.3. PCA

A Principal Component Analysis (PCA) was performed to explore possible correlations between hydrochemical (nitrate, TOC, electrical conductivity, dissolved oxygen), isotopic variables ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) and OCs (Pyrene, ΣPhACs , $\Sigma\text{pesticides}$ and $\Sigma\text{drugs of abuse}$) data to discriminate sources and processes (Fig. 5). The analysis accounted for the whole dataset (19 water samples) and ten variables that were selected after several analysis attempts. The first two principal components (PCs) explain 65.8% of the global variance of the analyzed data. Eigenvectors

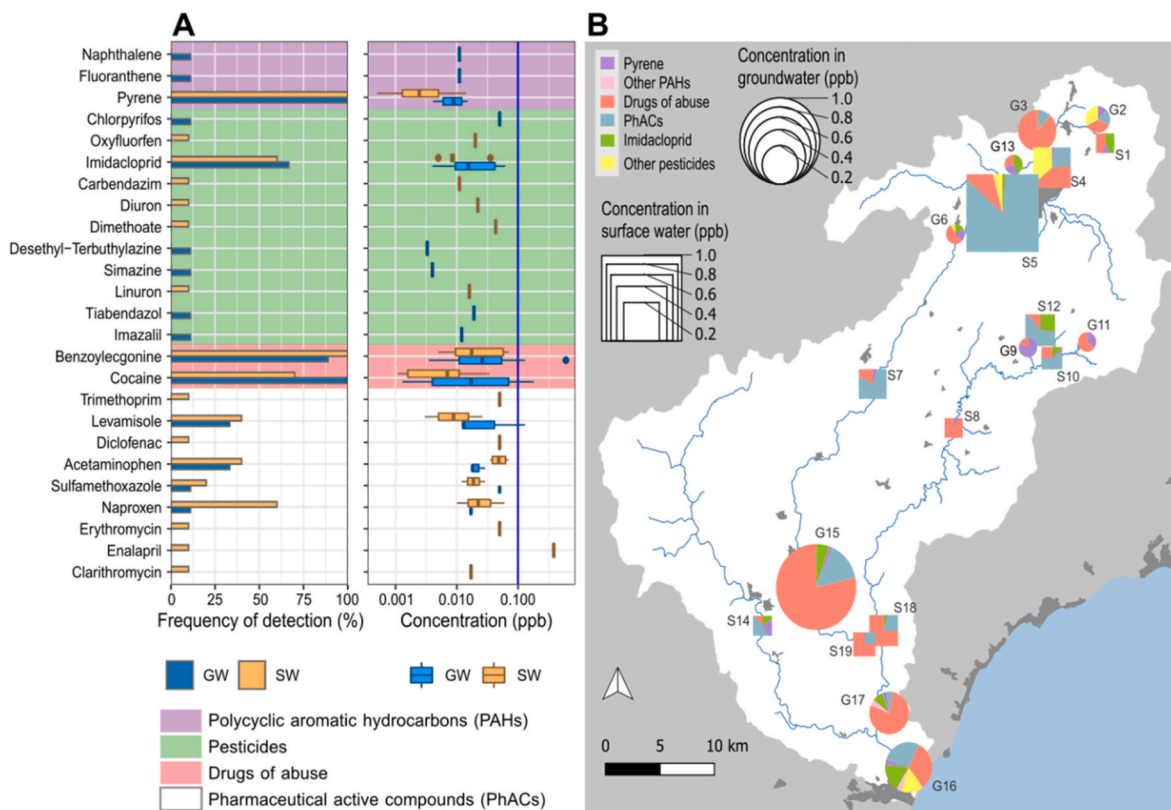


Fig. 4. (A) Frequency of detection (%) and boxplots showing concentration of organic contaminants detected in surface water (SW) and groundwater (GW) of the Guadiaro River basin. For comparison, vertical blue line is the EU limit for individual pesticides in groundwater (0.1 $\mu\text{g/L}$; European Parliament and the Council of the European Union, 2006); (B) pie charts of detected organic contaminants according to usage group in groundwater (circles) and surface water (squares). Size of circles and squares indicate the total contaminants concentration.

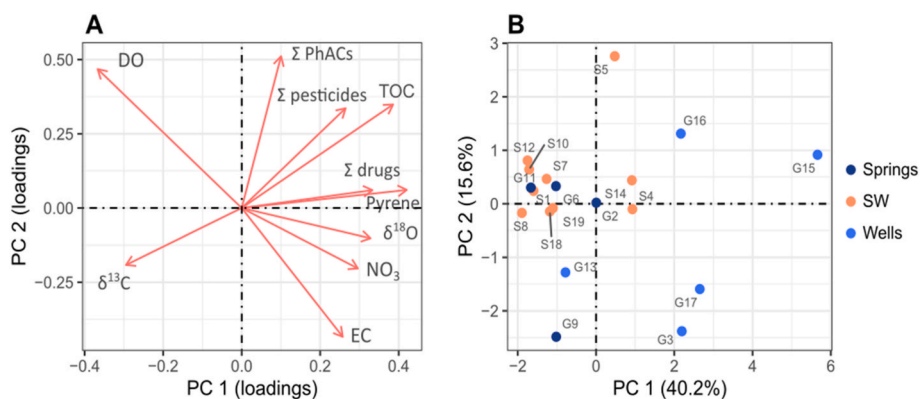


Fig. 5. PCA computed on samples collected from wells, springs and surface water (SW) courses: (A) PCA loading plot and (B) score plot with indicated variance explained by each Principal Component (%).

are displayed in Fig. 5a. PC1 is mainly defined by DO, Pyrene, Σdrugs of abuse, δ¹⁸O and δ¹³C; PC2 is mainly defined by ΣPhACs and EC (Table S5). PCA score plot (Fig. 5b) reveals that most surface water samples along with samples collected from springs are placed on the negative side of PC1 meaning that pumping wells are generally more polluted, except for sampling point S5, which showed a great concentration of PhACs (Fig. 4b) due to the proximity of the Ronda’s WWTP outlet.

4.4. Risk quotients

Three CECs were detected above the EU limits set for pesticides in groundwater (0.1 µg/L; European Parliament and Council of the European Union, 2006, Fig. 4): cocaine and benzoylecgonine, and levamisole (anti-helminthic drug), which suggests some hazard. Aside of this, a risk quotient approach (ECB, 2003) has been applied, thus considering the

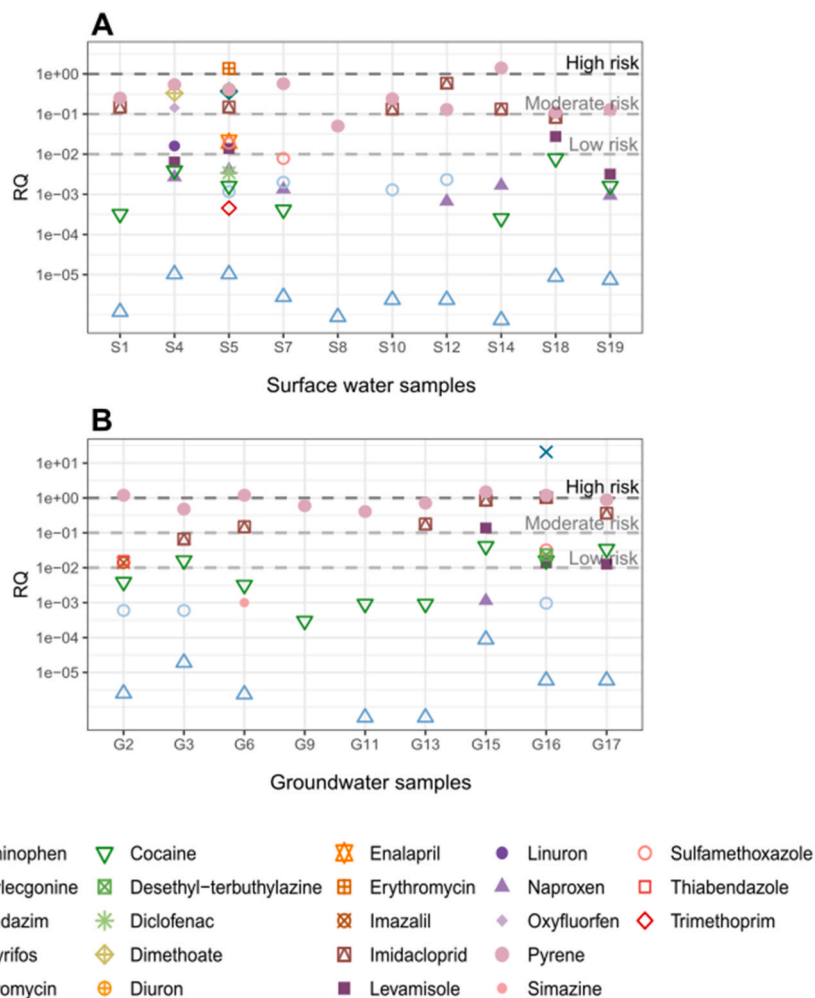


Fig. 6. Risk quotients (RQ) for detected organic contaminants in surface water (A) and groundwater (B) samples. Ecotoxicological data (for algae, invertebrate and fish) of each pollutant was gathered from literature (Table S2) and the lowest endpoint found was used for the RQ calculation.

potential ecological impact in surface water. Ecotoxicological data (for algae, invertebrate and fish) derived from literature is shown in Table S2 and it has been used to calculate the risk quotients (RQ). For the RQ calculation, the lowest endpoint available in the literature was used considering that the ecosystem sensitivity depends on the most sensitive species.

Given the connection between the monitored groundwater bodies and the surface water courses (as exposed in section 2.1. and as it will be further discussed in the following sections) and since concentration of OCs were generally higher in groundwater than in surface water (Fig. 4a), RQ have also been calculated for groundwater samples (Fig. 6b) to yield an overview of the worst-case scenario for the rivers and streams. It is called the *worse-case scenario* because in general some dilution is expected in the rivers fed by springs outflows or by groundwater flow in detrital aquifers connected to gaining rivers. Regarding surface water, if RQ is greater than one, the substance is of concern and further action should be taken by the competent authorities (ECB, 2003). Additional criteria applied by other authors for interpreting RQ in risk assessment studies have been used: “low risk” for $0.01 \leq RQ < 0.1$ and “medium risk” for $0.1 \leq RQ < 1$ (Sánchez-Bayo et al., 2002; Hernandez et al., 2006; Biel-Maeso et al., 2018). Only pyrene in sampling point S14 and antibiotic erythromycin in sampling point S5 showed a RQ above one even though erythromycin did not surpass the maximum admissible concentration for surface water indicated in the recently proposed list of priority substances in the EU (European Commission, 2022c). Erythromycin is an antibiotic with a strong capacity to inhibit growth in *Selenastrum capricornutum* (a microalgae; Eguchi et al., 2004), which increases its risk quotient given its measured concentration in water. In general, RQ increases for pyrene, cocaine and imidacloprid in groundwater with respect to surface water because of a higher concentration in the groundwater samples. A significantly high RQ for pesticide chlorpyrifos ($RQ = 21$) was estimated for sampling point G16.

5. Discussion

5.1. Distribution of OCs in water resources

The general presence of the organic contaminants throughout the water basin is a consequence of a widespread distribution of wastewater

discharging points (Fig. 2b) and it cannot be said that the mere absence of water treatments is the major reason for the presence of the pollutants: sample S5 showed the second greatest content in target pollutants ($0.8 \mu\text{g/L}$) among all samples. It was collected in the Guadiaro River, 1.7 km downstream from the Ronda’s WWTP outlet, reflecting the inefficiency of conventional water treatments to remove this type of compounds.

The first sample collected after S5 ($0.8 \mu\text{g/L}$ of total detected OCs) is S7, with $0.1 \mu\text{g/L}$ of total detected OCs. This pollution decrease can be caused by dilution. The Líbar mountain range (Fig. 1) has several outlets discharging towards the Guadiaro River, e.g., the Benaoján spring (sampling point G6). The EC value registered in G6 during the monitoring campaign was $261 \mu\text{S/cm}$. Jiménez-Gavilán et al. (2003) characterized the hydrodynamic functioning of the main springs of the Líbar mountain range and observed that the EC in the Benaoján spring fluctuated between 320 and $270 \mu\text{S/cm}$, approximately, following the dry and wet season conditions, respectively. Thus, the value registered in G6 during the monitoring campaign of this study reflects a response to rainwater recharge. This response generally occurs within one day or less after an important rain event (Jiménez-Gavilán et al., 2003). An increase of water draining through the spring can contribute to the dilution in the Guadiaro River, also promoted by the rain. Indeed, a slight increase in the Guadiaro and Hozgarganta River flow was registered during the monitoring campaign (Fig. 7). The decrease of EC downstream the Benaoján spring discharge (EC in S7 was $383 \mu\text{S/cm}$) with respect to the sampling points upstream (EC in S5 was $609 \mu\text{S/cm}$) also suggests a dilution process (Fig. 3).

Sampling point G15 shows the greatest score for PC1 in the PCA (Fig. 5b) since it presented the greatest content in detected OCs ($0.99 \mu\text{g/L}$). This was a pumping well drilled in the Quaternary aquifer made of alluvial sediments and located in the lower part of the basin (Fig. 1). Infiltration from the riverbeds is a water source in this part of the aquifer (Morales-García, 2007). However, the pollution content of surface water samples taken before (S7) and after (S19) the location of sampling point G15 was significantly lower (Fig. 4b). The explanation for this can be twofold: (i) the groundwater undertakes a reconcentration process and (ii) there is another pollution source in the aquifer, e.g., the soil. Wastewater discharges into the Guadiaro riverbed are known to happen before the location of point G15 (Fig. 2b), providing the surface water

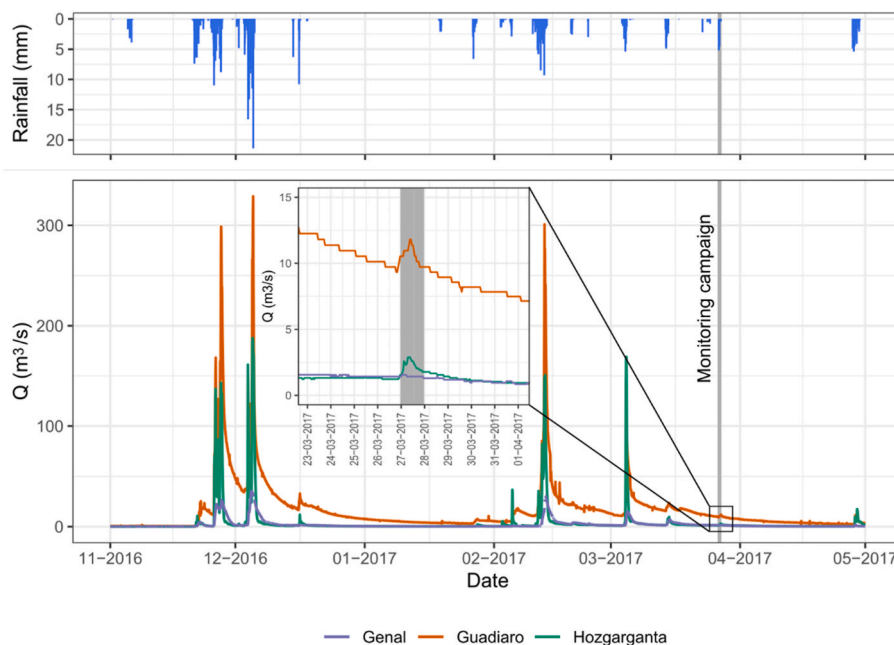


Fig. 7. Daily rainfall and flow rate evolution of the rivers Guadiaro, Hozgarganta and Genal (period 01/11/2016–01/05/2017; Hidrosur, 2022). Dark gray line indicates when the monitoring campaign of this study took place.

with a new contamination composition, i.e., that of sample S19, which is very similar to that of sample G15: organic compound analysis showed that cocaine, benzoylecgonine, naproxen, acetaminophen and pyrene were present in both samples (G15 and S19), but with higher concentration in the groundwater sample (Table S3). Nonetheless, G15 additionally presented a detectable content of the pesticide imidacloprid. A reconcentration process caused by irrigation return flows would increase the concentration of the PhACs and drugs of abuse. This process is also suggested by the water isotopes: the isotope composition of G15 is more enriched ($\delta^{18}\text{O} = -5.6\text{‰}$; $\delta^2\text{H} = -31.7\text{‰}$) than samples S7 and S19 ($\delta^{18}\text{O} = -6.4\text{‰}$; $\delta^2\text{H} = -37.2\text{‰}$ and $\delta^{18}\text{O} = -6.0\text{‰}$; $\delta^2\text{H} = -34.9\text{‰}$, respectively) and they form an evaporation water line in a $\delta^{18}\text{O}$ - $\delta^2\text{H}$ plot (Fig. S1). Water loss to evaporation during irrigation can lead to isotope enrichment due to isotope fractionation in the irrigation return flows thus increasing the $\delta^{18}\text{O}$ of the groundwater (Urresti-Estala et al., 2016; Llamas-Dios et al., 2021). The additional presence of the pesticide imidacloprid in groundwater can be a consequence of the washing of the soil by the irrigation return flows, since pesticides are normally applied on cultivated areas, which can be found on the flatlands over the alluvial Quaternary aquifer. This idea is supported by a rather negative value of $\delta^{13}\text{C}$ (-15.5‰ ; Table S4). $\delta^{13}\text{C}$ of samples S7 and S19 was -11.8‰ and -12‰ , respectively. When water infiltrates to the subsurface, it equilibrates with soil CO_2 . In most temperate land-scapes, $\delta^{13}\text{C}$ of soil CO_2 is about -23‰ (Clark and Fritz, 1997), which diminishes $\delta^{13}\text{C}$ of the infiltrating water. As anticipated by the position of G16 and G17 in the PCA score plot (Fig. 5b) and in the $\delta^{18}\text{O}$ - $\delta^2\text{H}$ plot (Fig. S1), re-pumping and irrigation return flows also affect these sampling points. However, a greater pollution of sampling point G15 with respect to G16 and G17, also drilled in the Quaternary aquifer of the lower basin, can be due, on the one hand, to the variable thickness of the aquifer formation: a 2.5 m thickness has been observed in the north part of this aquifer, shortly after San Pablo de Buceite village (Fig. 1), and the alluvial aquifer can be more than 50 m thick after the confluence of the Genal and Guadiaro rivers (Morales-García, 2007). This can limit the dilution of contamination within the aquifer in the upper part and can contribute to the accumulation of OCs. On the other hand, while river water mostly infiltrates into the aquifer in its northern part, the aquifer feeds the riverbed in the lower part (Junta de Andalucía, 2021b; Millán, 2022).

The PCA loading plot (Fig. 5a) showed that the electrical conductivity is poorly correlated with variables of OCs. EC can also be very representative of the geology and hydrogeology settings (e.g., dissolution/precipitation of minerals naturally present in the rocks) and not only of anthropogenic pollution (e.g., fertilizers can contribute to EC through dissolved ions such as sulphate). G9 was the sampling point with the lowest content in OCs and with the highest EC registered ($1302 \mu\text{S}/\text{cm}$). G9 (La Zúa spring) is a permanent spring in the Internal Zone outcrops of the Jarastepar mountain range (Fig. 1). La Zúa spring drains water from longer and shorter flow paths. De la Torre et al. (2020) determined that the relatively high concentration in sulphate (Fig. 3) in this outlet come from dissolution of gypsum from the Triassic evaporitic materials of the basement, meaning that the high EC is related to the lithology. They also observed that $\delta^{13}\text{C}$ in La Zúa spring varied from -5.0 to -10.4‰ , where the least negative value was attributed to a piston flow effect (sharp water recharge pushes longer residence water towards the outflow) but the most negative values were recorded in general during recharge periods, possibly due to short residence flows coming from the unsaturated zone in the karstified External Zone materials, presenting a $\delta^{13}\text{C}$ value closer to that of the soil (-23‰ ; De la Torre et al., 2020; Clark and Fritz, 1997). The $\delta^{13}\text{C}$ value recorded in G9 for this study was -7.9‰ , very similar to the mean value for the three years period (-7.8‰) given by De la Torre et al. (2020), suggesting a mix of shorter and longer residence flows, which can explain the little content in OCs. This content in OCs in G9 is largely represented by pyrene, a persistent pollutant that is more likely to remain in the aquifer for longer. The other springs sampled for this study are G2, G6 and G11. G2 and G6 showed a slightly higher and more diverse content in

pollutants in accordance with their higher vulnerability to contamination and proximity to anthropogenic activities. G2 (Ventilla spring) drains the south-western sector of the Merinos-Colorado-Carrasco aquifer system and a relatively high concentration of NO_3^- ($10.9 \text{ mg}/\text{L}$) is attributed to the agricultural activities and scattered buildings over the Miocene materials within its recharge area and close to this spring (Barberá-Fornell, 2014). The karst aquifer drained by G6 (Benaoján spring) presents well-developed karst landforms enhancing water infiltration and increasing its groundwater pollution vulnerability. These landforms include poljes where rain easily generates surface run-off that ends up drained by swallow holes. The presence of settlements without sewage systems and agricultural activities on these poljes areas makes them risky for groundwater quality (Andreo et al., 2006). The Igualeja spring (G11), with less detected OCs (Fig. 4b) is one of the main springs of Las Nieves mountain range aquifer system, which is very vulnerable to contamination due to a high degree of karstification, but just a limited number of polluting activities are located on the system mainly because of its protection status (Liñán-Baena, 2007, Fig. 2).

A negative correlation is observed between $\delta^{13}\text{C}$ and pyrene, Σ pesticides and Σ drugs of abuse (Fig. 5a). This relation is more evident for $\delta^{13}\text{C}$ -pyrene in most surface water samples (Fig. 8a). This can indicate a remobilization of the pollutants previously stored in the soil or subsurface by surface runoff (e.g., generated by rainfall) that finally reaches the water courses. Reiman and Jun-Xu (2019) attributed the $\delta^{13}\text{C}$ decrease correlated with the increase of the river flow, due to the arrival of the wet season, to flushing of soil CO_2 and organic matter from the catchment. An inverse correlation between the variables TOC (Total Organic Carbon) and $\delta^{13}\text{C}$ (Fig. 5a) supports this theory. Infiltration and aquifer recharge can also reduce the $\delta^{13}\text{C}$ signal of groundwater because of the more depleted $\delta^{13}\text{C}$ value of the soil (Clark and Fritz, 1997). The $\delta^{13}\text{C}$ signal of surface water is overall higher than that of groundwater (Fig. 8) due to its contact with the atmosphere: atmospheric CO_2 had a $\delta^{13}\text{C}$ of -8.5‰ in 2017 (Scripps Institution of Oceanography, 2022). Besides, removal of CO_2 by photosynthesis contribute to a more enriched $\delta^{13}\text{C}$ in surface water (Atekwana and Krishnamurthy, 1997).

Pyrene stood out as the compound with the highest frequency of detection: it was found in all water samples, but at low concentration (Fig. 4). PAHs are mainly produced by incomplete combustion of organic materials such as coal, oil, petrol and wood (Maletić et al., 2019). The occurrence of pyrene throughout the Guadiaro River basin can be attributed to stubble-burning, an activity limited to the areas out of the protection status (Fig. 2a), but also to forest fires, which are relatively frequent in the region (Fig. 9), followed by atmospheric transport, deposition and remobilization with surface run-off, as suggested by $\delta^{13}\text{C}$. PAHs are volatile enough to evaporate and deposit, and long-range atmospheric transport occur depending on their physico-chemical properties (Wania and Mackay, 1996). Four-ring PAHs, such as pyrene, present a relatively low mobility in the global environment, meaning that they tend to deposit and accumulate in mid-latitudes, whereas, for instance, less ringed PAHs would rather deposit in polar latitudes (Wania and Mackay, 1996). The fact that pyrene was detected in less than 10% of water samples in catchments located to the west of the Guadiaro River basin, with high agricultural activity, during similar studies (Llamas-Dios et al., 2021; Llamas et al., 2022) suggests that forest fires can contribute more to the presence of pyrene in this case. There has been an increasing loss of forest mass especially in the center part of the basin and surrounding areas due to fires (i.e., Bermeja mountain range; Figs. 1 and 9): between 1817 and 1991, fires occurred every 14.5 years on the north face of the Bermeja mountain range; between 1975 and 2018 fires occurred approximately every 6 years (Martos-Martín and Gómez-Sotano, 2021). Most fires took place in the south and east of the Guadiaro River basin (Fig. 9). Predominant winds in the Málaga province during summer come from the Mediterranean Sea (southeast; Capel-Molina, 1999) and in general there is little influence from the Atlantic Ocean in the Guadiaro River basin

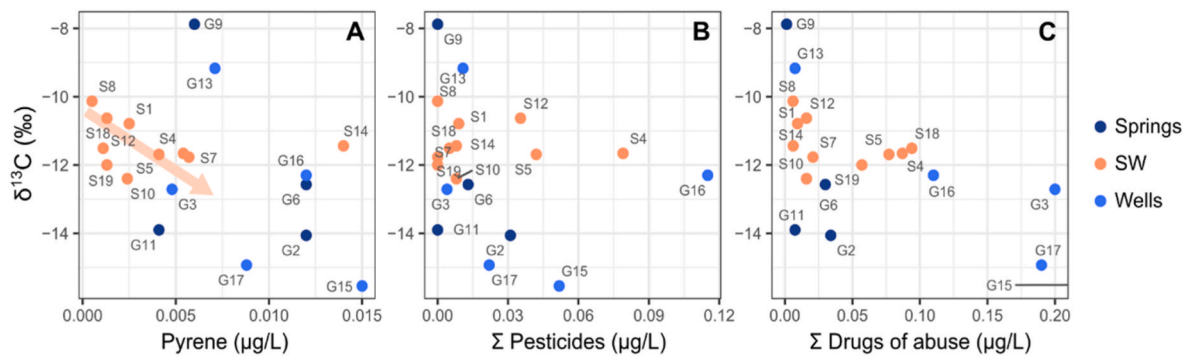


Fig. 8. Biplots showing the relation between $\delta^{13}\text{C}$ and pyrene (A), Σ pesticides (B) and Σ drugs of abuse (i.e., cocaine and benzoylecgonine; C) in monitored springs, wells and surface water (SW). Note: $\delta^{13}\text{C}$ and Σ drugs of abuse of well G15 are -15.5‰ and $0.78 \mu\text{g/L}$, respectively.

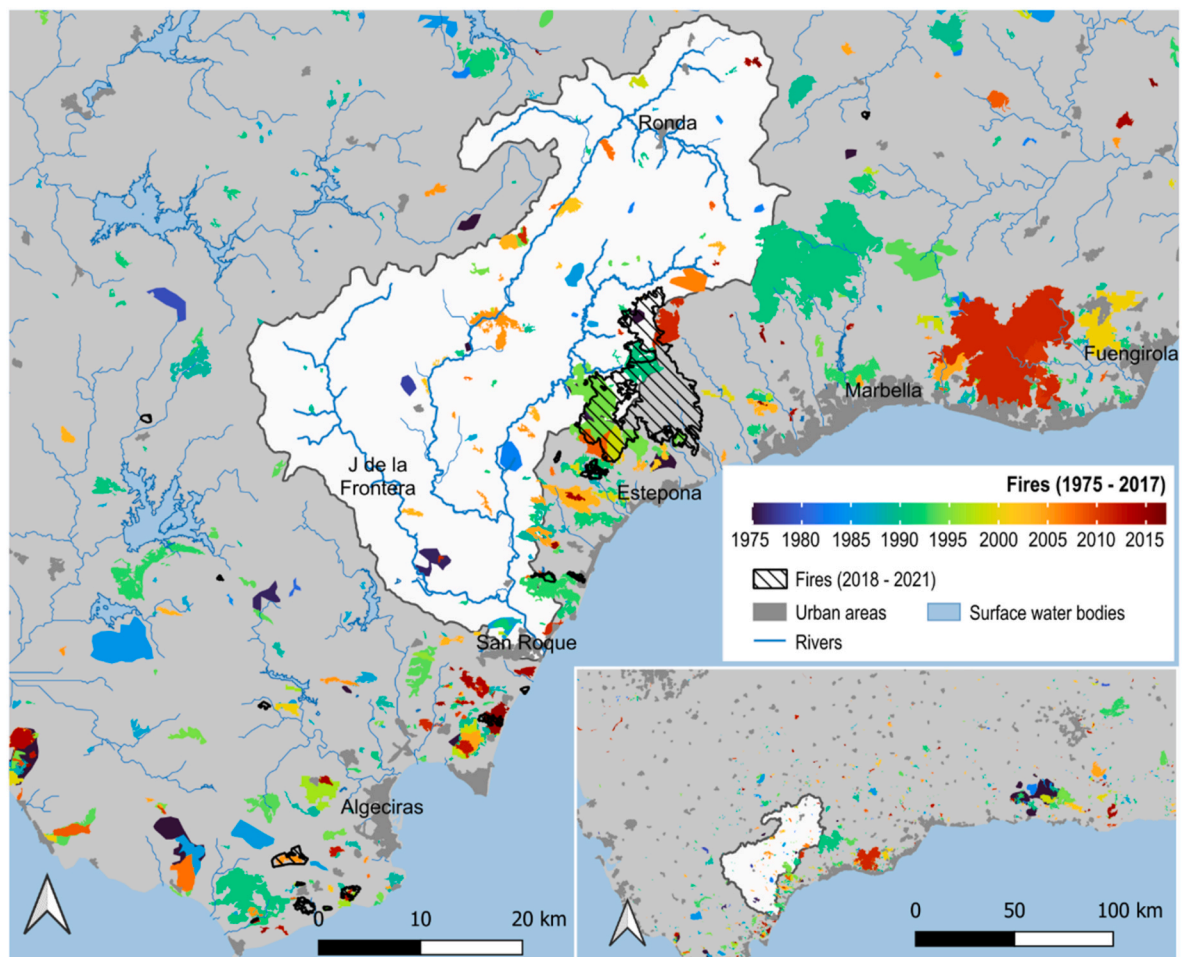


Fig. 9. Forest fires in the Guadiaro River basin and surrounding areas from 1975 to 2017 (before the sampling campaign of this study; colored) and from 2018 to 2021 (Junta de Andalucía, 2021c).

because of orographic barriers in the west (Jiménez-Gavilán, 2011). Studies have been conducted to evaluate the occurrence and temporary variation of PAHs in surface water and occasionally in groundwater after a wildfire in Mediterranean areas: Vila-Escalé et al. (2007) and Mansilha et al. (2019) observed a decrease of detected PAHs over time after the fire but later peaks of PAHs in water occurred following the precipitation profile, indicating a remobilization of PAHs stored in sediments. Vila-Escalé et al. (2007) analyzed 18 PAHs species over fifteen months after the fire in water and sediments, and pyrene remained at the highest concentrations near the end of the monitoring period, suggesting a

greater persistence in the environment. Monitoring of water quality should continue in order to evaluate the impact of the fires that took after this study (i.e., in 2021 almost 10,000 ha burned at the southeast of the basin; Fig. 9).

5.2. Environmental risk assessment

Results obtained in the risk assessment are useful to overview the risk that the OCs may entail for the environment. However, they should be taken cautiously since they correspond to exposure to single

contaminants and considering ecotoxicological effects on algae, invertebrates and fish, such as growth inhibition (Eguchi et al., 2004), immobility (Kim et al., 2007), metabolism reduction or mortality (Isidori et al., 2005). Synergetic effects are not reflected in RQ. For instance, Eguchi et al. (2004) observed that the presence of the antibiotic trimethoprim significantly enhanced the growth inhibition action of the antibiotic sulfamethoxazole in algae, which would increase the ecological threat in sampling point S5, with both compounds present (Fig. 6a). Cocaine and benzoylecgonine were two of the most frequently detected pollutants in both surface water and groundwater but at relatively low concentrations. Hence, no risk of cocaine nor benzoylecgonine has been elucidated from comparing the measured concentrations in the study area with available ecotoxicological data in the literature, which was, however, very scarce. RQ does not consider the pollutants bioaccumulation that might have been going on before the sampling and that could enhance the toxicity. It is accepted that compounds with octanol/water partition coefficients ($\log K_{ow}$) equal to or greater than 3 may bioaccumulate (ECB, 2003), which would be the case for pyrene ($\log K_{ow}$ of pyrene = 4.88; Kim et al., 2019). Imidacloprid (insecticide) showed a moderate risk in six out of the ten surface water samples collected. However, it is possible that this risk increases during summer months because of two reasons: (i) it has been observed that detection of insecticides in water resources increases at the beginning of the summer due to their typical application period (Herrero-Hernandez et al., 2017; Llamas et al., 2022) and (ii) river flow rate keeps decreasing (Fig. 7) thus dilution of incoming contaminants will be limited. Significant impacts on the flow rate in the middle and low reaches of the Guadiaro River can take place due to river water extractions for irrigation, urban supplies and hydroelectric exploitation (Junta de Andalucía, 2021a), thus dilution can be severely limited during the dry season (Fig. 7). The Genal river flow rate often lowers drastically at the low reach, before the confluence with the Guadiaro river, also due to water extraction for irrigation (Junta de Andalucía, 2010), a situation that can worsen the state reflected in sampling point S18, with pyrene and imidacloprid reaching moderate risk levels (Fig. 6a).

As mentioned, given the interaction between surface water and groundwater, RQ were also calculated for groundwater samples (Fig. 6b). This yields the worst-case scenario for water courses as some dilution is expected in the rivers fed by aquifers. However, as mentioned, this dilution can change greatly across seasons (Fig. 7). In general, RQ increases for pyrene, cocaine and imidacloprid in groundwater with respect to surface water because of a higher concentration in the groundwater samples. Most of the flow rate of the Ventilla stream (S1) comes from the water discharge of the Ventilla spring (G2), where pyrene reaches a $RQ > 1$. It has been exposed in a previous section how water discharges in the Líbar mountain range (e.g., Benaoján spring [G6]) into the Guadiaro River likely dilute the river water regarding the concentration of pharmaceuticals. However, the Benaoján spring (G6) showed a high risk for pyrene and a moderate risk for the pesticide imidacloprid. The quality impact of springs like Benaoján on the Guadiaro River likely increases at the end of the dry season, when first rain events in autumn in the Líbar mountain range causes a piston flow effect of the unsaturated zone, where salts have been accumulating during the dry season (Jiménez-Gavilán, 2011), as OCs might do as well (Luque-Espinar et al., 2015). Pyrene and imidacloprid also reach a $RQ > 1$ in G15, a pumping well used for irrigation in the middle-lower stretch of the Guadiaro River. Although some runoff generated by irrigation could reach the riverbed, in this part of the aquifer the main water transfer occurs from the river towards the groundwater table (Moral-García, 2007). In the lowest part of the Guadiaro river, close to the river mouth, the aquifer feeds the riverbed (Junta de Andalucía, 2021b; Millán, 2022). In this zone, the sampling point G16 showed a high risk for pyrene and imidacloprid and showed a significantly high RQ for pesticide chlorpyrifos ($RQ = 21$). This RQ is due to a relatively high concentration of this pesticide in this sampling point ($0.05 \mu\text{g/L}$) and to a low toxicity endpoint for *Chironomus riparius* ($LC_{50} = 0.024 \mu\text{g/L}$;

Table S2), a common invertebrate present as larvae in European rivers. Chlorpyrifos can no longer be used in the European Union since 2020 because of ecological and human health related concern (European Commission, 2020). Further research should elucidate if this pesticide is still being used in this zone where the aquifer is feeding the surface water course or what compounds are being used nowadays to replace it. As mentioned, the flow rate in the middle and low reaches of the Guadiaro river can suffer greatly from river water extractions (Junta de Andalucía, 2021a), which lower the dilution capacity. In these situations, the composition of the groundwater of the feeding aquifers will mostly mark that of the river.

6. Conclusions

Organic contaminants (including contaminants of emerging concern have been monitored in the little anthropized basin of the Guadiaro river and they have been detected in all water samples. Detected OCs included polycyclic aromatic hydrocarbons (i.e., pyrene), drugs of abuse (i.e., cocaine and its metabolite), pharmaceuticals and pesticides.

Results have suggested that an intense exploitation of groundwater of main detrital aquifers covered by irrigated crops potentially contribute to a re-concentration of contaminants within the aquifer through irrigation return flows. The slower water dynamic of detrital porous aquifers with respect to that of carbonate karstic aquifers also makes the accumulation of OCs a more feasible process.

The environmental risk assessment showed low or no risk for aquatic organisms of most of the contaminants detected in surface waters according to available ecotoxicological data. Among these, cocaine and benzoylecgonine (detected in 84% and 95% of water samples, respectively) showed no risk to aquatic organisms, based on very scarce toxicological data.

In general, pyrene, detected in 100% of water samples, showed a moderate risk to aquatic life in surface water. Calculated risk quotients of pyrene increased in groundwater. Its widespread occurrence throughout the basin is attributed to atmospheric deposition and forest fires have been pointed out as a potential origin. Given the environmental persistence of this type of compounds and the relatively high frequency of forest fires in the area, the presence of pyrene could be considered a continuous pressure in the study basin.

Samples were taken at the end of March. Given that wastewater discharges are expected to remain largely the same, the emerging contaminants (i.e., drugs of abuse and pharmaceuticals) will likely reach higher risk quotients during summer months, as dilution capacity of the rivers will decrease, until the arrival of the rainfalls. This is also expected for insecticides, which are most often applied in June. Moreover, as river flow declines over the dry season, groundwater input from springs in carbonate aquifers and from lateral groundwater flow in detrital aquifers will gain relevance in marking the composition of rivers. This could also increase the RQ for some OCs (i.e., pyrene and pesticide imidacloprid) in the rivers since concentration of detected contaminants were generally higher in groundwater. RQs will also likely increase with the first rain events in autumn, that will cause the remobilization of the contaminants that would have been accumulating in the soil, as suggested by $\delta^{13}\text{C}$.

7. Recommendations

The obtained results provide important information for water resource management and for future research practices.

Eliminating water quality threats in the middle reach of the Guadiaro River by implementing water treatments should be a priority since river water extractions can diminish dilution greatly at this point and because, downstream, the river infiltrates in a part of the aquifer where re-concentration of the pollutants in groundwater is likely to occur due to smaller aquifer dimensions. Ronda's WWTP is the largest pollution source in the area and setting up tertiary treatment could decrease CECs

risks to aquatic organisms in the receiving water course (Yang et al., 2017; Ravikumar et al., 2022).

The conductance of subsequent monitoring campaigns and risk evaluations should be encouraged considering the significant fires that took place after the monitoring campaign of the present study.

Further research shall verify the launched hypothesis and address the limitations of this piece of work: The monitoring network can be extended to improve representativeness. Analyzing more surface water samples would better define the relationship between OCs and $\delta^{13}\text{C}$. More groundwater samples in the detrital aquifers would allow to characterize the observed re-concentration of pollutants likely due to irrigation return flows and see how this process varies depending on the thickness of the aquifer. Monitoring campaigns performed over time would be necessary to better characterize the OCs response to the change of hydrodynamic conditions.

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CRediT authorship contribution statement

M.I. Llamas: Writing – original draft, Investigation, Methodology, Writing – review & editing, Visualization, Formal analysis. P.J. Fernández-Valenzuela: Investigation, Formal analysis. I. Vadillo: Funding acquisition, Project administration, Supervision, Conceptualization, Investigation, Methodology, Data curation, Writing – review & editing. M. Sanmiguel-Martí: Methodology, Data curation. J. Rambla-Nebot: Methodology, Data curation. J.L. Aranda- Mares: Methodology, Data curation. P. Jiménez-Gavilán: Conceptualization, Methodology, Supervision, Data curation, Writing – Review & Editing.

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.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2023.118903>.

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