



Multivariate analysis of organic contaminants in groundwater of an endorheic basin draining to a salt lagoon – Fuente de Piedra (Southern Spain)

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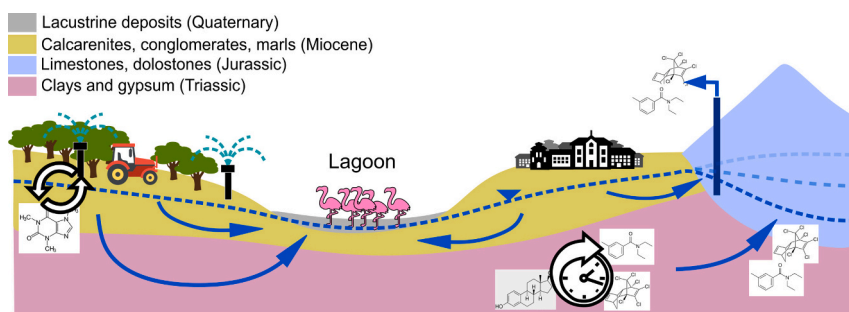
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HIGHLIGHTS

- OCs can be preserved in deep and saline conditions in evaporitic aquifer.
- Overexploitation of carbonate aquifer may lead to OCs transfer from adjacent aquifers.
- Potential re-concentration of OCs due to irrigation return flows

GRAPHICAL ABSTRACT



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ABSTRACT

Forthcoming EU environmental requirements on water resources quality are likely to include concentration limits of certain contaminants of emerging concern, such as pharmaceuticals and personal care products. However, understanding the occurrence of organic contaminants, including contaminants of emerging concern, in hydro(geo)logical media remains challenging. This study is based on a comprehensive screening of OCs in groundwater of the unique and complex Fuente de Piedra Lagoon endorheic basin system using hydrochemistry and isotopic tools. The basin includes interconnected aquifers of various types (detrital, carbonate and evaporitic). Groundwater recharges the hypersaline lagoon, which holds significant ecological value, but is heavily impacted by anthropogenic activities such as water exploitation for urban supply and irrigation, soil fertilization for agricultural activities and urban wastewater discharges. Out of 185 analyzed compounds, 32 were detected, including 6 personal care products, 10 antibiotics and 11 pharmaceuticals. Concentrations ranged from 0.1 ng/L to 974 ng/L. Notably, the pesticide aldrin was detected with a maximum concentration of 668 ng/L. Two main processes are suggested as potentially affecting the occurrence of different groups of organic contaminants: (i) re-concentration of the more mobile compounds due to irrigation return flows in the unconfined detrital aquifer and

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(ii) accumulation of certain contaminants in the deep, saline underground media within the evaporitic aquifer, which forms the geologic basement of the detrital and carbonate aquifers of the basin. This study highlights the difficulty in understanding the occurrence of organic contaminants in complex systems and underscores the challenge of meeting the forthcoming environmental requirements.

1. Introduction

Contaminants of emerging concern (substances derived from human consumption and activities such as pharmaceutical active compounds, personal care products, substances derived from industries, among others) are drawing increasing attention due to their potential adverse effects on living beings and their ubiquity in the environment, particularly in aquatic systems (Bunting et al., 2021; Wilkinson et al., 2022). On the 26th of October 2022, the European Union Commission published a proposal for the amendment of the Water Framework Directive (2000/60/EC), the Groundwater Directive (2006/118/EC) and the Directive on Environmental Quality Standards (2008/105/EC) in which the list of priority substances is extended (European Commission, 2022a). Some emerging contaminants are included in this list, such as certain antibiotics, estrogenic hormones, and other pharmaceuticals (European Commission, 2022b).

The distribution of organic contaminants (OCs), including contaminants of emerging concern, in subsurface environments is difficult to understand since it can be affected by different factors, such as the location of pollution sources, the hydro(geo)logical characteristics of the given environment, including sediment texture and lithology (Lutri et al., 2020), hydrodynamic conditions (Corada-Fernández et al., 2017; Llamas et al., 2023), and the physico-chemical properties specific to each OC, which influence their susceptibility to natural attenuation. Retention of non-ionizable compounds (or neutral species of ionizable chemicals) in the soil is determined by hydrophobic sorption onto uncharged soil organic matter (Schaffer and Licha, 2015). Hence, the octanol-water partition coefficient ($\log K_{ow}$) is a useful parameter, as it indicates the degree of hydrophobicity of a chemical (Jurado et al., 2022). Overall, the higher the tendency of OCs to be sorbed onto soil particles (organic matter, clay, oxides; Appelo and Postma, 2005), the lower their bioavailability, and thus the more they will persist in the environment (Clarke and Smith, 2011). However, a continual release of chemicals through sewage discharges into the aquatic environment is thought to be offsetting the degradation rates, even of the more unstable OCs (Daughton, 2004).

The Fuente de Piedra (FP) lagoon is a seasonally variable hypersaline lagoon in a closed drainage, i.e., endorheic, basin in southern Spain. The high salinity of the FP lagoon is due to evaporation processes and groundwater discharges from an evaporitic confined aquifer that constitutes the basement of the basin (Montalván et al., 2017). Because of the great biodiversity of the FP lagoon, its ecological importance has been recognized at a regional, national and international level: it was one of the first Spanish wetlands included in the Ramsar Convention in 1983; it was declared a Nature Reserve in 1984 and a Special Protection Area for Birds in 1987. The FP lagoon is the second most important breeding site for *Phoenicpterus ruber* in the Western Mediterranean zone after La Camargue, in France (Heredia-Díaz et al., 2007). OCs, including contaminants of emerging concern, have been detected broadly in aquifers and watercourses of the Guadalhorce River basin, adjacent to the FP basin, and other surrounding areas (Llamas-Dios et al., 2021; Llamas et al., 2022, 2023). Studying the presence of OCs in the aquifers of this endorheic basin is important since the FP lagoon is largely recharged by groundwater (Linares, 1990; Montalván et al., 2017). Furthermore, the aquifers are exploited for urban water supply and agriculture, which has impacted water quality and quantity severely for two decades (Rodríguez-Rodríguez et al., 2016; González-Báez et al., 2018).

Studies on the presence of OCs at aquifer/basin scale have been

performed including inland and coastal detrital aquifers (e.g., Avisar et al., 2009; Candela et al., 2016; Sassine et al., 2016; Boy-Roura et al., 2018), carbonate karstic aquifers (Reberski et al., 2022) and volcanic aquifers (e.g., Estévez et al., 2016; Gasco-Cavero et al., 2023). To the best of the authors' knowledge, no study on the presence of emerging contaminants in hydrogeological systems including hypersaline environments has been conducted, presumably because water resources in this type of geologic media are not suitable for human consumption. However, it is still important to assess the potential pollution of such hydrogeological environments, especially if they are connected to dependent ecosystems and potentially affect other water resources, as described in this case study. No examples of studies about OCs in endorheic basins have been found either in the literature.

The presence of a wide array of OCs (185 analytes) in groundwater was meticulously studied to unravel the causes of their spatial distribution in the complex hydrogeological system of the endorheic basin and its hypersaline FP lagoon (which includes three interconnected aquifers of different nature and strong affection by human activities, i.e., exploitation for urban supply and irrigation, soil fertilization for agricultural activities and urban wastewater discharges) using hydrochemistry and isotopic tools. The main goal is to contribute to understanding the fate and transport of OCs in endorheic areas which often display complex surface-groundwater interactions and hydrogeological dynamics.

2. Methods

2.1. Study area: geography and geology

The FP lagoon is a hypersaline wetland (roughly 11 mS/cm) comprising an area of 13.5 km² and located in an endorheic catchment (150 km²) in the south of the Iberian Peninsula, in Spain (Fig. 1). The altitude of the basin varies from 410 m a.s.l. (in the location of the lagoon) to up to 798 m a.s.l. at the summit of the Molina mountain range. The Humilladero mountain range, also located at the boundaries of the catchment (Fig. 1), reaches an altitude of 680 m a.s.l. (Linares, 1990). Mean annual precipitation is 460 mm, with the wettest period occurring between November and February (mean values can reach up to 70 mm/month) and July being the driest month (mean values are most often <5 mm/month). The mean annual temperature is 17 °C, with potential evapotranspiration reaching an average value of 830 mm per year (Heredia-Díaz et al., 2007).

Geologically, the catchment is located within the external area of the Baetic Cordillera. Three main aquifer types can be distinguished (Fig. 1): (I) unconfined aquifers lodged in Jurassic and Cretaceous carbonate blocks corresponding to the Humilladero and Molina mountain ranges (permeability in these formations is due to fissures and karstification); (II) an unconfined porous aquifer formed by Quaternary deposits and Upper Miocene calcarenites and sandstones (Heredia-Díaz et al., 2007) and (III) an evaporitic confined aquifer formed within the olistostrome of the Chaotic Sub-baetic Complex (CSC; Middle Miocene). The latter is a karstic-type aquifer formed by blocks of limestones and dolostones from the Jurassic to the Oligocene Era confined by a clayey, marly and salty (gypsum and halite) matrix from the Upper Triassic period (Montalván et al., 2017). It constitutes the almost impermeable basement of several closed basins throughout the region, such as the FP basin, the dissolution of its karstifiable materials being considered the cause of the subsidence of these basins (Kohfahl et al., 2008). The aforementioned aquifer systems in the endorheic catchment of interest are hereafter referred to as

carbonate, Mio-Quaternary and CSC aquifer, respectively. The thickness of the Mio-Quaternary aquifer is estimated to be <30 m throughout most of the basin area; however, the greatest thickness (> 40 m) is found in the surroundings of the town of Fuente de Piedra and to the north of the town of Humilladero, where there is also a higher proportion of coarse sediments and thus, a higher permeability (Fig. S1; Heredia et al., 2009; Linares, 1990). The thickness of the carbonate aquifers is around 300 m and 450 m in the case of the Molina and Humilladero mountain ranges, respectively (Martos-Rosillo et al., 2013).

2.2. Hydro(geo)logical dynamics of the study basin: conceptual model

The conceptual model of the groundwater system in this basin has been described as follows (Kohfahl et al., 2008; Montalván et al., 2017): water recharge in the upper system (carbonate and porous aquifers)

occurs locally, and groundwater flows from these recharge spots toward the lagoon. Water recharge of the CSC aquifer comes from infiltration of rainwater through the outcropping materials (Fig. 1), and indirectly through discharge from the carbonate blocks and the Mio-Quaternary aquifer groundwater. The CSC aquifer discharge occurs locally (toward the lagoon) and regionally (through hypersaline springs in the adjacent Guadalhorce River basin). Two main streams flow into the lagoon, Santillán and Arenales (Fig. 1), which nowadays are seasonal, mostly due to an increase of groundwater exploitation. A mixing process takes place underneath the lagoon with the freshwater discharge in convection cells resulting in recycled brines that are led back up toward the lagoon by the fresher flow.

Water resources within the endorheic basin (i.e., Mio-Quaternary and carbonate) are used mainly for irrigation (16 hm³/year, approx.; Junta de Andalucía, 2021), with olive trees covering most of the basin

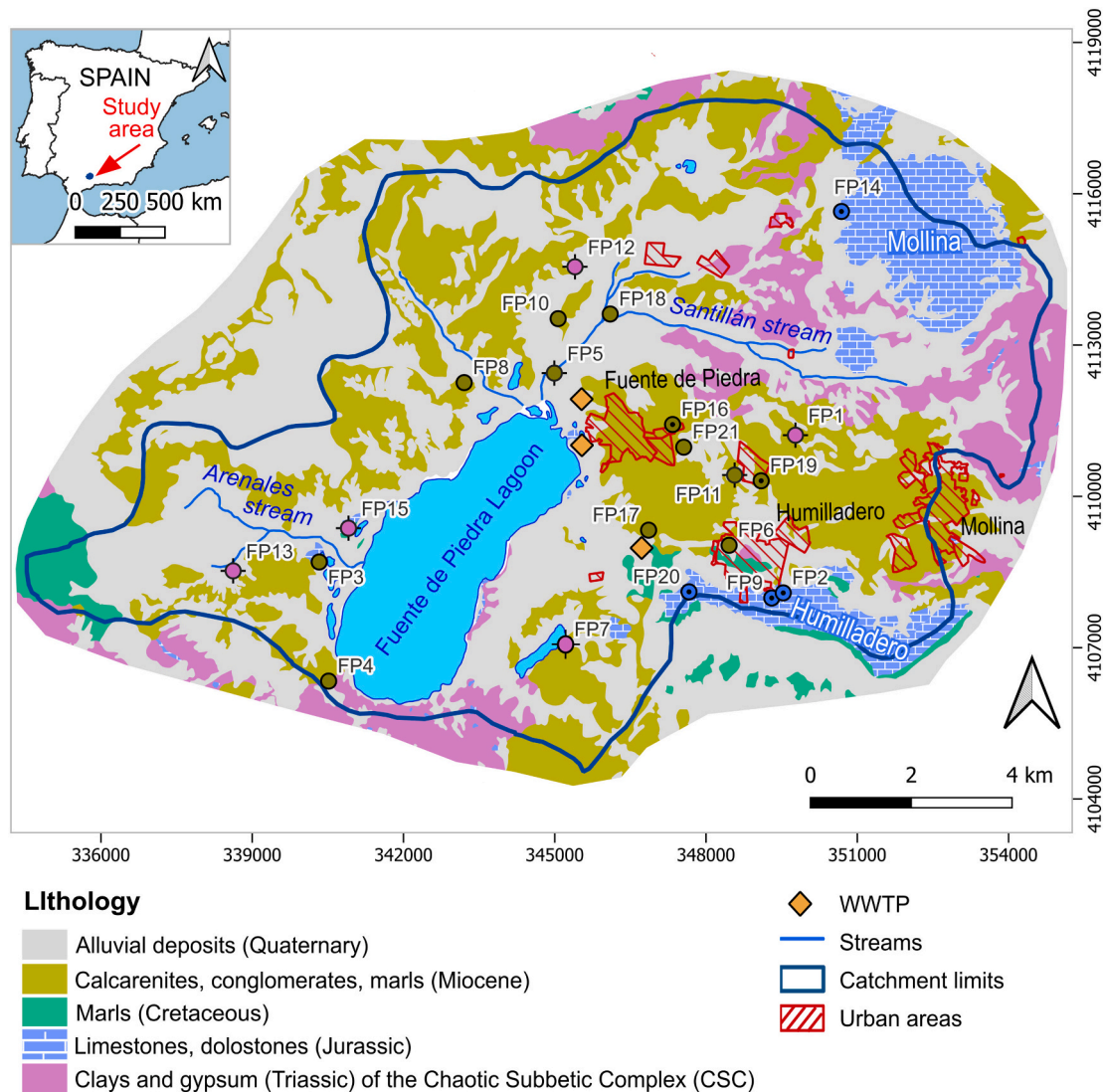


Fig. 1. Fuente de Piedra lagoon catchment and location of sampling points (monitoring campaign conducted in April 2018). To estimate which wells and piezometers reached the CSC aquifer, their depths were obtained from the Spanish Geological Survey database (IGME, 2021; Table S1) and compared to the Mio-Quaternary thickness estimated in Heredia et al. (2009; Fig. S1). ‘WWTP’ means Waste Water Treatment Plant.

area (Fig. S2). Water resources are also used for urban water supply ($3 \text{ hm}^3/\text{year}$ approx.), industry and livestock farming ($0.17 \text{ hm}^3/\text{year}$; Junta de Andalucía, 2021). Overexploitation jeopardizes the Mio-Quaternary and carbonate aquifers, resulting in their piezometric levels dropping over time, more dramatically in the case of the carbonate ones (Rodríguez-Rodríguez et al., 2016). Intensive groundwater pumping in the carbonate aquifers has broadly reversed the groundwater flows. Under wet and natural conditions (with most wells inactive), the piezometric contour lines indicated a radial groundwater flow that converged toward the lagoon (Fig. 2B). Under (over)exploitation conditions, two cones of depression in the Mollina and the Humilladero mountains have developed (Fig. 2B). Hence, the Miocene aquifer is now recharging the Jurassic blocks in some sectors, which is worsening the water quality in the carbonate aquifer (Rodríguez-Rodríguez et al., 2016; González-Báez et al., 2018). An increase in salinity and a migration from a bicarbonate water type toward a sodium chloride type has been observed over the last two decades (Fig. 2A).

The FP lagoon receives the discharges of three WWTPs of the two towns within the basin (Fuente de Piedra and Humilladero). Water purification treatment of the Humilladero WWTP (the one further to the south) consists of primary treatment and lagooning. Purification in the

first WWTP of the town of Fuente de Piedra (the one further to the north) consists of primary and secondary treatment, and the second WWTP of the town of Fuente de Piedra includes primary and secondary treatment and lagooning. The application of reclaimed sewage sludge (biosolids) to agricultural lands is a potential source of OCs in the region. However, little data is available about current patches of land receiving biosolids since controls over this practice by the water basin authority are still recent (BOJA, 2018). Other potential sources of OCs include some livestock production sites in the southeast of the basin (Fig. S2), fertilization with manure and slurry, as is the case in adjacent catchments (Urresti-Estala et al., 2015; Llamas-Dios et al., 2021), and leakages from septic tanks and sewerage systems of the urban areas.

2.3. Hydrochemical and isotopic analysis

A sampling campaign was conducted in April 2018 and consisted in the collection of 21 groundwater samples (Fig. 1). Most samples were taken from open wells and piezometers (Fig. 1) using a bailer. Sampling points FP2, FP14 and FP20 are pumping wells located in the carbonate aquifers used for urban water supply. The sampling campaign was conducted during the recharge season (Fig. S4).

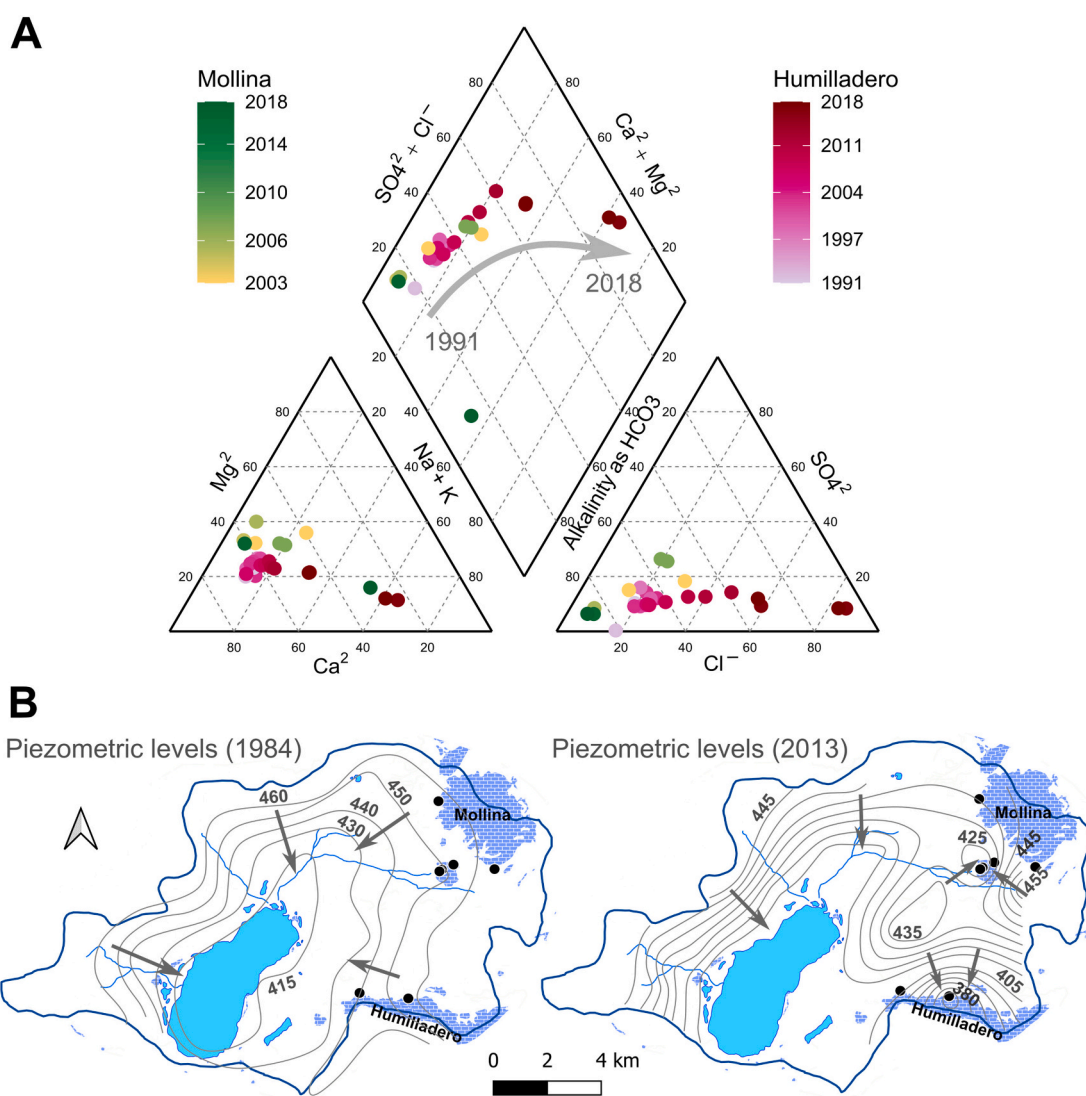


Fig. 2. (A) Piper plot showing the composition of groundwater from the carbonate aquifers of the Humilladero mountain range (1991–2018) and the Molina mountain range (2003–2018; data from Montalván et al., 2017; González-Báez et al., 2018 and own databases), and (B) maps showing piezometric contour lines in 1984 (natural conditions) and 2013 (during overexploitation; modified from Martos-Rosillo et al., 2013). Black dots on the maps indicate points where samples were taken for hydrochemistry analysis and are plotted in the Piper diagram (A).

Samples for hydrochemical and isotopic analysis were stored in sterile high-density polyethylene bottles (120 mL) sealed with inverted cone caps. Samples for organic compound analysis were stored in sterile amber glass bottles (1 L) with Teflon caps. All bottles were rinsed before sampling, transported in a cool-box in darkness and stored in a fridge ($<4^{\circ}\text{C}$) until analysis. Samples for organic compounds were filtered and analyzed within 24 h after sampling. Water physico-chemical parameters (temperature, electrical conductivity, pH, redox potential and dissolved oxygen) were measured during fieldwork with a portable multi-parameter probe (Hach-Lange HQ40d; Hach Loveland, CO, USA).

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

As regards organic compounds, the analytical methods applied included 185 analytes belonging to different compound categories: pharmaceutical active compounds (PhACs), personal care products (PCPs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organophosphate esters flame retardants and plasticizers (OPEs) and pesticides. PhACs (including analgesics, anti-inflammatories, lipid regulators, psychiatric drugs and stimulants, β -blockers, and antibiotics among others; see Table S1) were determined by solid-phase extraction followed by ultra-performance liquid chromatography–triple quadrupole mass spectrometry using a Bruker EVOQ Elite system (Bruker, Billerica, MA, USA) equipped with an electrospray ionization source (Baena-Nogueras et al., 2016). PCPs (including insect repellents, UV filters, fragrances, antibacterials and plasticizers), PAHs, PCBs and OPEs and pesticides were analyzed using stir bar sorptive extraction (Pintado-Herrera et al., 2014) followed by gas chromatography (SCION 456-GC, Bruker), coupled with triple quadrupole mass spectrometry (SCION TQ from Bruker with CP 8400 Autosampler; Pintado-Herrera et al., 2016). These analyses were conducted in the laboratory of the Marine Research Institute of the University of Cádiz. A list of analyzed organic compounds and more details about the analytical methods for organic compounds are provided as Supplementary Material (Table S1).

2.4. Geochemical modelling and statistical analysis

The PHREEQC code was used to calculate the state of saturation (saturation index) for calcite. The Pitzer database was used for the calculations of samples with an ionic strength higher than 0.5 (Appelo and Postma, 2005). A correlation matrix (Pearson method) and a Principal Component Analysis (PCA) were performed using the 'stats' package in R software (R Core Team, 2021) to explore relationships between selected variables and to identify driving background processes (Kovács et al., 2012). PCA reduces the dimensionality of datasets by creating new uncorrelated variables (Principal Components; PCs) from the original variables. Before conducting the PCA, the dataset was z-score standardized. PCA results are reflected in a loading plot (the factor loadings are the correlation coefficients between the PCs and the original variables) and a score plot (PC scores are the transformed variable corresponding to each data point; Liu et al., 2017). The correlation matrix was displayed using the 'ggcorrplot' package in R software (R Core Team, 2021).

3. Results and discussion

3.1. Hydrochemistry and isotopic composition

Hydrochemical data and measured electrical conductivity (EC) resulting from the April 2018 campaign are represented using Stiff

diagrams in Fig. 3. These results are also available in the Supplementary Material (Table S3 and Fig. S3).

Water samples taken from piezometers reaching the CSC materials show a calcium chloride (FP1) and a sodium chloride type composition (Fig. 3), which reflects the dissolution of the evaporitic material of this formation and the influence of deeper and longer residence times of water flows as opposed to those from the Mio-Quaternary aquifer. EC values of these samples range between 1107 $\mu\text{S}/\text{cm}$ (FP15) and 19,920 $\mu\text{S}/\text{cm}$ (FP1; Table S3). FP15 is a 157 m deep piezometer displaying rather low mineralization values as it crosses a calcareous block and only reaches the CSC formation at a depth of 155 m (Heredia et al., 2009), whose evaporitic nature leads to a sodium chloride facies.

Samples from the Mio-Quaternary aquifer have a calcium-magnesium chloride-sulphate type composition (Fig. 3) and EC ranging between 905 and 6110 $\mu\text{S}/\text{cm}$ (Table S3). Given the high exposure of this aquifer to diffuse pollution sources (i.e., agriculture fields; Fig. S2), nitrate content is high, ranging between 20.6 and 194.2 mg/L, with a mean value of 97.9 mg/L. Nitrate pollution also affects most of the other sampling points but to a lesser extent, as shown by the mean value of nitrate found in carbonate and CSC sampling points (46.4 and 46.5 mg/L, respectively). No nitrate was detected in FP1, and the FP15 nitrate concentration was 0.4 mg/L, likely due to reductive conditions, since measured dissolved oxygen was low in both points (around 2 mg/L; Table S3).

Samples from the carbonate aquifers show different hydrochemical water types. Samples FP2 and FP9 have a calcium-magnesium chloride type composition and an EC of 1697 and 2290 $\mu\text{S}/\text{cm}$, respectively, while sample FP20 displays a sodium chloride type composition and 5660 $\mu\text{S}/\text{cm}$ (Fig. 3; Table S3). This high mineralization is potentially due to the induced recharge of the carbonate aquifer from the Mio-Quaternary formation, as previously explained. Sample FP14 displays an EC of 486 $\mu\text{S}/\text{cm}$ and is of sodium bicarbonate-type composition, which suggests that fresh water is flushing salt water from the aquifer (Appelo and Postma, 2005). The latter would be consistent with the fact that the monitoring campaign (April 2018) was conducted during the recharge season (Fig. S4). Aside from FP14 (Mollina carbonate aquifer), water types displaying better quality are those of Mio-Quaternary points located to the east of the lagoon and to the north of the town of Humilladero (Fig. 3), where the Mio-Quaternary formation is thicker (Fig. S1).

Water stable isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$) obtained of the samples range from -6.6 ‰ to -4.6 ‰ for $\delta^{18}\text{O}$ and from -44.7 ‰ to -27.9 ‰ for $\delta^2\text{H}$. The isotopic composition of the water samples are depicted in Fig. 3B, and most samples show enriched isotopic values relative to the Global Meteoric Water Line (GMWL: $\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$; Craig, 1961), with most samples aligned according to a slope of 5.2. This indicates water losses to evaporation potentially induced by continuous re-pumping for irrigation and return flows, given the strong presence of agricultural activities in the basin (Fig. S2).

3.2. Detected organic contaminants (OCs)

Thirty-two OCs were detected out of the 185 analyzed, as follows: two polycyclic aromatic hydrocarbons, one pesticide, ten antibiotics, 11 PhACs of other kinds (including two estrogens), six personal care products and two industrial products: nonylphenol and tributylphosphate (TBP-N). Frequencies of detection and concentrations are shown in Fig. 4. Frequencies of detection are high, with 12 contaminants detected in >75 % of the samples, 15 were detected in >50 % of the samples and 22 were detected in >25 % of samples. Concentrations range from 0.1 ng/L to 974 ng/L. The concentrations of all detected OCs are available in the Supplementary Material (Table S4 and S5).

Several contaminants stand out due to their elevated detected concentration and/or widespread occurrence, including the pesticide aldrin, sulfonamides sulfathiazole, sulfamethoxazole, sulfamethizole and sulfadiazine, fluoroquinolones norfloxacin and danofloxacin, the

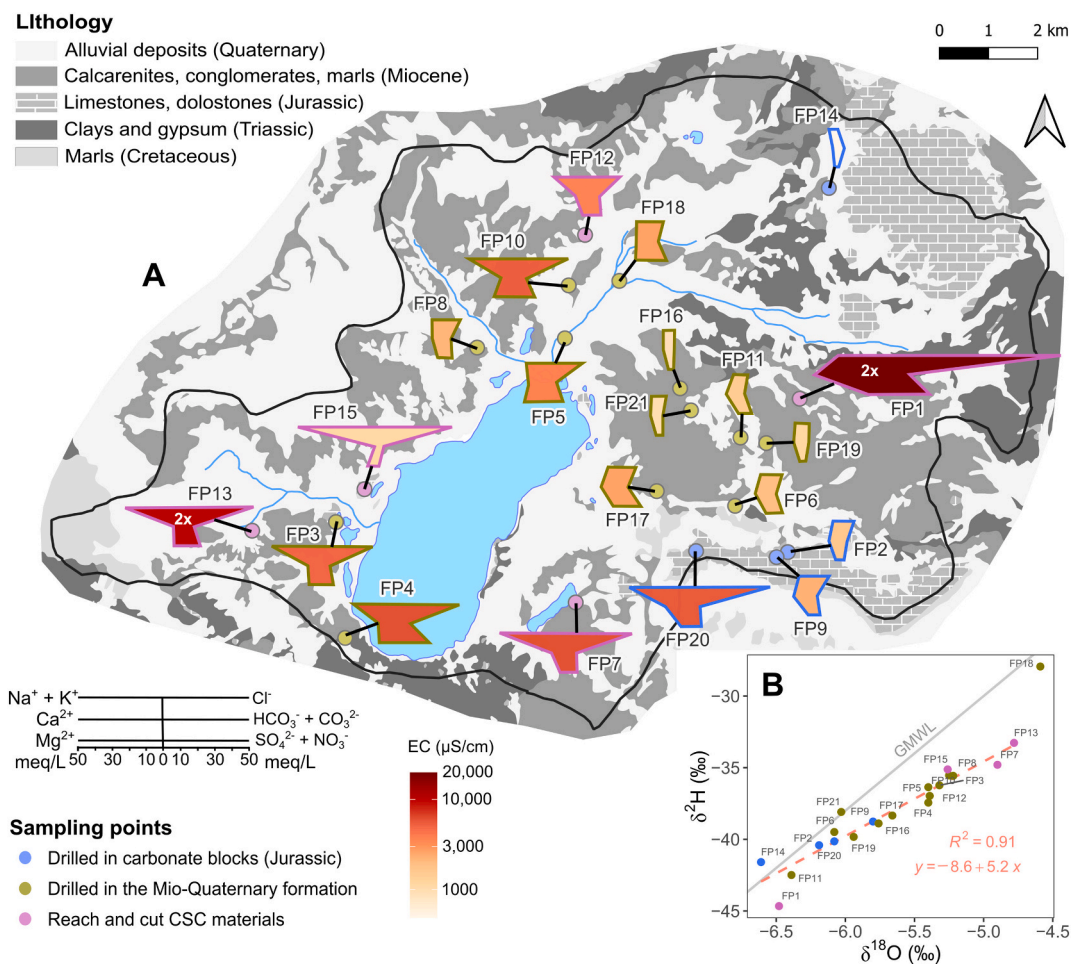


Fig. 3. (A) Stiff diagrams of groundwater samples collected in April 2018 and (B) stable isotopes ($\delta^{18}\text{O}$ - $\delta^2\text{H}$) of groundwater samples. Electrical conductivity (EC) is indicated by the fill color of Stiff diagrams.

stimulant caffeine, estrogens 17 β -estradiol (E2) and 17 α -ethynyl estradiol (EE2), the antibacterial triclosan and the insect repellent DEET.

Insecticide aldrin, with an average concentration of 318.5 ng/L, largely exceeded the limit established by the EU for pesticides in groundwater (100 ng/L; European Parliament and Council of the European Union, 2006) in seven out of the nine sampling points in which it was found (Table S5). The use and production of aldrin is banned in Europe (European Parliament and Council of the European Union, 2019). Therefore, the occurrence of this substance can be due to historical use (at least prior to its ban in Spain in 1991; BOE, 1991) and its high hydrophobicity and persistence rather than current use. Caffeine was detected in >95 % of the samples with an average concentration of 112.8 ng/L. It is one of the most reported compounds globally in groundwater (Lapworth et al., 2012). Caffeine is very mobile in groundwater because it tends to remain in the aqueous phase since, under environmental pH conditions, it has a neutral form (Kim et al., 2019) and shows a low k_{ow} (-0.07; Biel-Maeso et al., 2018). Its widespread presence is potentially due to the fact that it is produced in large quantities (OECD, 2004). Antibiotics sulfathiazole, sulfamethazole and sulfadiazine were detected in all samples, with average concentrations of 0.5, 17.7 and 2.5 ng/L, respectively. The antibiotics danofloxacin and norfloxacin (fluoroquinolones) were detected in 86 and 90 % of the samples, respectively, with an average concentration of 58.6 ng/L and 94.1 ng/L, respectively. Sulfonamides and fluoroquinolones are widely used for animal care (Leal et al., 2013). The presence of sulfonamides in water has been widely reported, especially sulfamethoxazole (Barnes et al., 2008; López et al., 2015; Lapworth et al., 2012), which can be due

to their low biodegradability (Boy-Roura et al., 2018). A concentration of 10 ng/L of sulfamethoxazole, detected in >95 % of samples in this study, was suggested as a groundwater quality standard by the EU Commission (European Commission, 2022b). This limit was exceeded in two samples (Table S4). Fluoroquinolones, e.g., norfloxacin and danofloxacin, show high sorption capacity mainly through the cation exchange mechanism (Leal et al., 2013), which can contribute to accumulation in the subsoil and to a higher concentration. However, norfloxacin and danofloxacin are not frequently detected in groundwater studies (Barnes et al., 2008; Candela et al., 2016; Corada-Fernández et al., 2017; Boy-Roura et al., 2018). A concentration of 250 ng/L of carbamazepine was also suggested as a groundwater quality standard (European Commission, 2022b). Carbamazepine was detected in three samples out of 21 and the maximum concentration detected was 5 ng/L. The suggested concentration limit of total PhACs in groundwater (250 ng/L; European Commission, 2022b) is exceeded in 14 of the 21 samples collected, with a maximum concentration of total PhACs of 1802 ng/L. Antibacterial triclosan was detected in all water samples, with an average concentration of 40.9 ng/L. Triclosan is a commonly reported Personal Care Product in groundwater studies (Lapworth et al., 2012). It was detected in >80 % of samples of surface and groundwater in the Guadalhorce basin, adjacent to the FP basin (Llamas-Dios et al., 2021). In the proposal for amendment of the water Directives, triclosan was not added as a groundwater quality standard but as a priority substance in surface waters, whose proposed maximum allowed concentration is 20 ng/L, which is exceeded in all samples of this study (Table S5). Thus, the limit proposed for surface water is widely exceeded

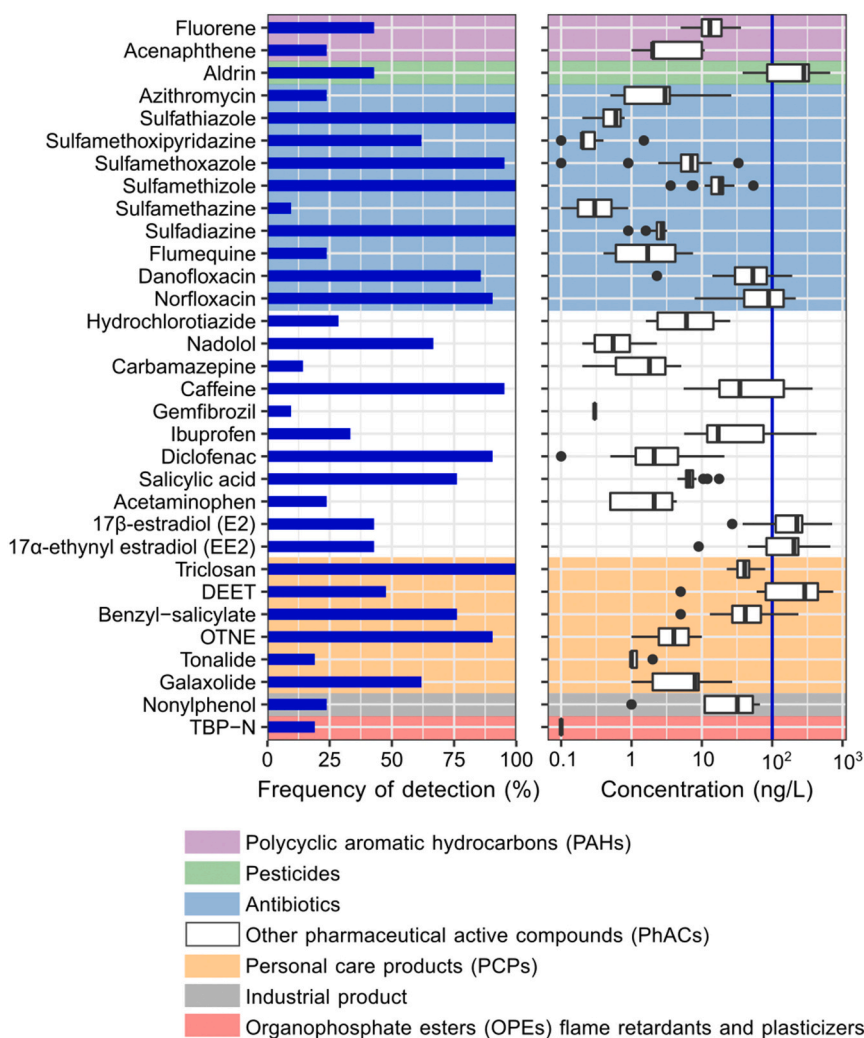


Fig. 4. Frequency of detection and box plot of concentration for organic contaminants found in groundwater samples in the Fuente de Piedra basin (April 2018). For comparison, the vertical blue line is the EU limit for individual pesticides in groundwater (100 ng/L; European Parliament and Council of the European Union, 2006).

in groundwater, and this is of concern, as the recharge of the lagoon comes mostly from groundwater (Linares, 1990). The occurrence of the detected DEET and estrogens are discussed in the following sections.

3.3. Spatial distribution of detected OCs

The spatial distribution of the OCs detected sorted by groups is shown in Fig. 5. No evident spatial pattern can be observed. The sampling points with the largest OC total content (> 1300 ng/L) are FP1 (CSC), FP2 (carbonate), FP12 (CSC), FP13 (CSC), FP15 (CSC) and FP16 (Mio-Quaternary). Given the fact that OCs are found at relevant concentrations to the west and to the south of the lagoon, and thus far from the influence of urban areas and their WWTPs, sources other than sewer leakages and wastewater discharges need to be considered, i.e., irrigation and fertilization with livestock slurry and manure (Ghirardini et al., 2020) in addition to reclaimed sewer sludge (biosolids; Clarke and Smith, 2011).

3.4. Data analysis: first overview of the relationships between OCs and hydrochemical and isotopic variables

The relationship between selected OCs and hydrochemical parameters has been explored using a correlation matrix (Fig. 6A). The selected OCs have been those with a frequency of detection higher than 40 %. The selected hydrochemical parameters were those that can be

representative of different processes or origins, including anthropogenic activities like agriculture or wastewater release (NO_3^- , Total Organic Carbon, K^+), re-concentration by evaporation due to irrigation return flows ($\delta^{18}\text{O}$; Urresti-Estala et al., 2016; Llamas-Dios et al., 2021), soil washing by infiltrating rain water (pH, Saturation Index of calcite, TOC; Fig. S4), mineralization due to longer residence times of groundwater and influence of the CSC formation (Cl^- , Br^-).

The group of variables that are more significantly correlated are Ca^{2+} , Cl^- , Br^- and the organic contaminants benzyl-salicylate, DEET, 17 β -estradiol (E2), 17 α -ethynyl estradiol (EE2), and aldrin (Fig. 6A). There is also a correlation between Ca^{2+} , Cl^- , Br^- and the sum of the more hydrophobic OCs ($\log K_{ow} > 2$; Table S6), but this largely corresponds to the aforementioned substances, as they have been found at the highest concentrations (Fig. 4). Antibiotics norfloxacin and danofloxacin also show a correlation. Caffeine correlates with the fragrance galaxolide and with the anti-inflammatory diclofenac. A slight correlation is observed among antibiotics sulfadiazine, sulfathiazole, sulfamethoxazole, sulfamethizole and nitrate (Fig. 6A). These variables have been selected to perform a PCA (Fig. 6B and C).

The first two principal components (PCs) explain 62.4 % of the global variance of the analyzed data. Eigenvectors are displayed in Fig. 6C. PC1, which explains most of the variance (48.6 %), is mainly defined by aldrin, E2, EE2, DEET, benzyl-salicylate and Cl^- , which are largely found in CSC sampling points (Fig. 6B). These OCs have been selected for further discussion, given their significant correlations (Fig. 6A) and

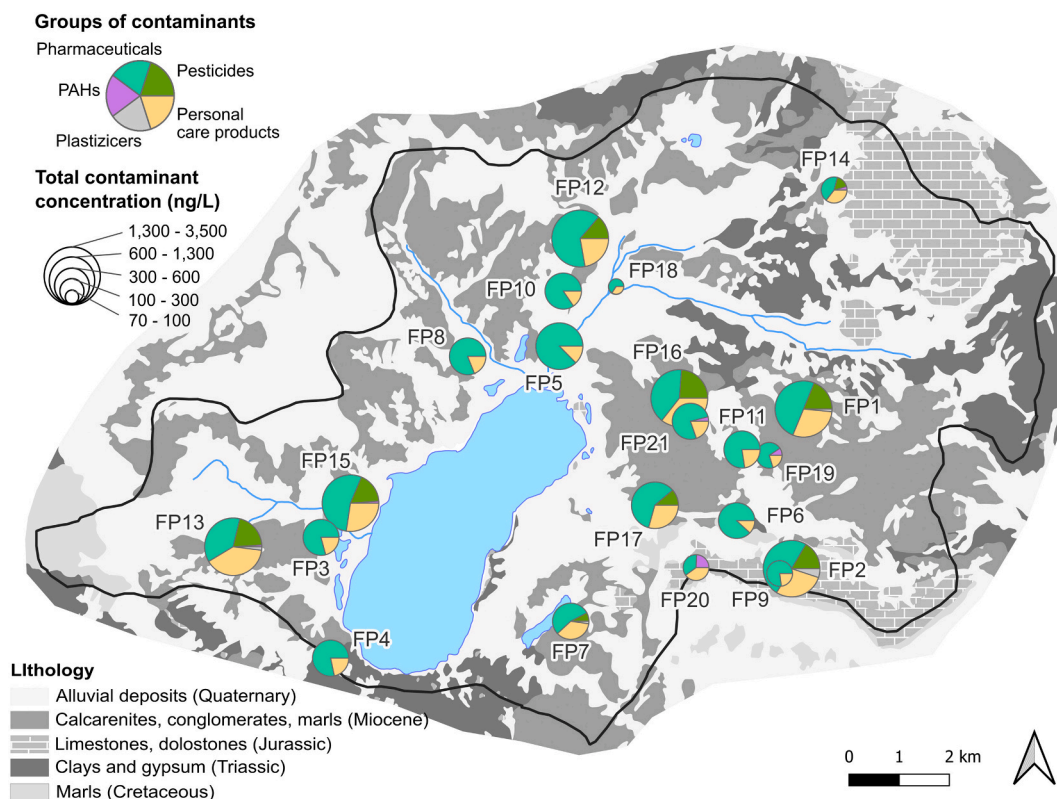


Fig. 5. Pie charts of groups of organic contaminants detected in groundwater sampling points in April 2018.

elevated concentration (Fig. 4).

PC2 (which explains 13.8 % of variance) is mainly defined by sulfadiazine, sulfathiazole, sulfamethoxazole and diclofenac (Fig. 6C). It can be observed that the sampling points most affected by antibiotics and nitrate are mainly those draining the Mio-Quaternary formation. The slight correlation between the selected antibiotics and nitrate (Fig. 6A and C) suggests that they largely share the source, which can be agricultural fertilization, since antibiotics are an important group of emerging contaminants carried by livestock manure and slurry (Ghirardini et al., 2020), which can be used to fertilize crops. The variables of galaxolide, caffeine and diclofenac are mainly drawn by FP15 (Fig. 6B), suggesting an exceptional situation caused potentially by the influence of a septic tank leakage from a nearby farming facility (Fig. S2).

3.5. Potential sources of selected OCs

E2 and EE2 are natural and synthetic estrogens, respectively. E2, among other estrogens, is naturally excreted by male and female humans and animals. The occurrence of EE2 in the environment is due to the use of birth control pills, in the case of human origin (Adeel et al., 2017). DEET is the most common main ingredient in insect repellents for human skin application, products like mosquito nets and also for pets (Merel and Snyder, 2016). Benzyl-salicylate is commonly used in fragrances and as a UV filter. Detected concentrations of estrogens in groundwater in this study (average of 252 and 276 ng/L for EE2 and E2, respectively; Table S4) are higher than what has been found in urban wastewater: Tang et al. (2021) reviewed the occurrence of EE2 in influents and effluents of municipal WWTP across 29 countries, indicating average concentrations for this substance of 78.4 ng/L and 12.3 ng/L, respectively. Regarding E2, Kumar et al. (2011) reported a mean influent and effluent concentration in 11 WWTPs in the UK of 43 ng/L and 13 ng/L, respectively. Reported concentrations of DEET and benzyl-salicylate in urban wastewater vary greatly. An average of 34.5 ng/L of

benzyl-salicylate has been detected in untreated wastewater in several locations in Romania, making it one of the least abundant among the ten analyzed UV filters of the study (Chiriac et al., 2021). Another study reported a mean concentration of 8960 ng/L with high daily variability (± 5320 ng/L) in the influent of a WWTP (Simonich et al., 2000). The presence of DEET in wastewater has been observed to be highly dependent on seasonality and location. Marques dos Santos et al. (2019) reported concentrations in inlets of 7 WWTP in different regions in the US across a two-year period, which ranged from 780 ng/L to 15,200 ng/L during the summer months. Biel-Maeso et al. (2019) monitored a wide range of PCPs in inlets and outlets of a WWTP (primary and secondary treatment plus UV radiation) in SW Spain over a year; concentrations of DEET in the inlet and outlet ranged from undetected to 683 ng/L and from undetected to 492 ng/L, respectively.

This difference between groundwater estrogen levels in this study and those reported in urban wastewater in the literature can reveal an accumulation process in the aquifers of the endorheic catchment and/or an additional source, such as the application of manure or slurry or biosolids to agricultural fields for fertilization. Pollution sources other than urban wastewater discharges or leakages from sanitation networks need to be considered, as OCs have been found to the west and to the south of the lagoon, where the groundwater sampling points lack urban areas or WWTP upstream. Indeed, the discharge of estrogens to the environment from livestock is estimated to be twice the human rate in the EU (Adeel et al., 2017). However, the role of biosolids as a contaminant source cannot be discarded. Estrogens are moderately hydrophobic ($\log K_{ow}$ of E2 and EE2 are 3.94 and 3.67, respectively; Adeel et al., 2017) and thus tend to be sorbed onto the sludges during wastewater treatment (Carballa et al., 2004). E2 has been detected in biosolids from an activated sludge municipal WWTP (230 ng/g; Andaluri et al., 2012). Despite the elevated DEET concentrations that can be observed in raw wastewater (Marques dos Santos et al., 2019), DEET is not found at high levels in biosolids, which is attributed to its relatively low $\log K_{ow}$ (2.02; Biel-Maeso et al., 2019), although it is still present. It was detected

hydrophilic (Table S6; Carballa et al., 2004).

3.6. Processes affecting the occurrence of OCs

Fig. 7 shows the main correlations between selected ions, between OCs, and between both. Mostly, high positive correlations can be observed, although FP1 has high leverage, in general.

In other studies, a correlation with the conservative ion Cl⁻ has been interpreted as a re-concentration process due to irrigation return flows (Llamas-Dios et al., 2021). However, in this case, because of the high influence of evaporites in the hydrochemistry of groundwater, Cl⁻ and Br⁻ ions may not reflect this process but the dissolution of minerals. Indeed, no evident correlation is observed between Cl⁻ and δ¹⁸O (Fig. 8A). In cases with no significant additional Cl⁻ source, Cl⁻ and δ¹⁸O often show a positive correlation in agricultural areas because irrigation return flows and subsequent re-pumping, i.e., recirculation, increases salinization due to evaporation, which also causes an enrichment in heavy isotopes, e.g., oxygen-18 (Urresti-Estala et al., 2016; Llamas-Dios et al., 2021).

The relationship between δ¹⁸O and the total concentration of the OCs with higher hydrophilicity, i.e., lower octanol-water partition coefficient (log K_{ow} < 2; Table S6), and the rest of the contaminants (more hydrophobic) is plotted in Fig. 8. In the δ¹⁸O vs Σ hydrophilic OCs plot, a positive correlation can be observed for those samples with δ¹⁸O < -5.5 ‰. These sampling points are in the east of the basin (Fig. 8D), where the Mio-Quaternary aquifer is thicker (Fig. S1) and where permeability within the detrital aquifer is higher due to changes in sediment texture (Martos-Rosillo et al., 2013). Hydrophilic compounds generally show a lower retardation factor compared to hydrophobic ones, being more

easily transported by the water flow (Boy-Roura et al., 2018) and thus, more easily affected by pumping. This is of importance since water resources are currently obtained from this zone of the Mio-Quaternary formation for urban supply, as water quality and quantity in the carbonate aquifers have been diminishing over the years.

The correlation of Cl⁻ and Br⁻ with contaminants benzyl-salicylate, DEET, E2, EE2 and aldrin can be explained by the presence of groundwater flows from the CSC aquifer. Indeed, these contaminants were only detected in wells FP1, FP2, FP7, FP12, FP13, FP15, FP16 and FP17, except for benzyl-salicylate, which was detected more broadly. These sampling points were among the deepest of the monitoring network (an exception is FP16 and FP17 whose depth is unknown; Table 1), in most cases reaching the CSC formation. The influence of CSC groundwater flows in pumping wells FP2 and FP14 (drilled in carbonate blocks) can occur through induced recharge from adjacent formations, as explained in previous sections (see Fig. 2). OCs can be attenuated in the surface thanks to biodegradation, especially in the soil, but this can be limited at deeper levels (Gasco-Cavero et al., 2023) due to the lower diversity of microorganisms and because of redox controls, which can potentially increase the residence time, i.e., persistence, of OCs as follows (Lapworth et al., 2012). For example, the half-life of EE2 and E2 has been estimated to be 81 and 2 days, respectively, in a groundwater system under aerobic conditions, whereas, under anaerobic conditions, the half-life of E2 can increase to 107 days and no degradation of EE2 has been observed (Ying et al., 2003; Adeel et al., 2017). Moreover, high salinity linked to groundwater flows in the CSC formation can contribute to limiting microbial growth and biodegradation (Khouni et al., 2023). Aldrin has an estimated half-life in soils of 1.5–5.2 years and more than half of the original weight converts to dieldrin, which is more resistant to

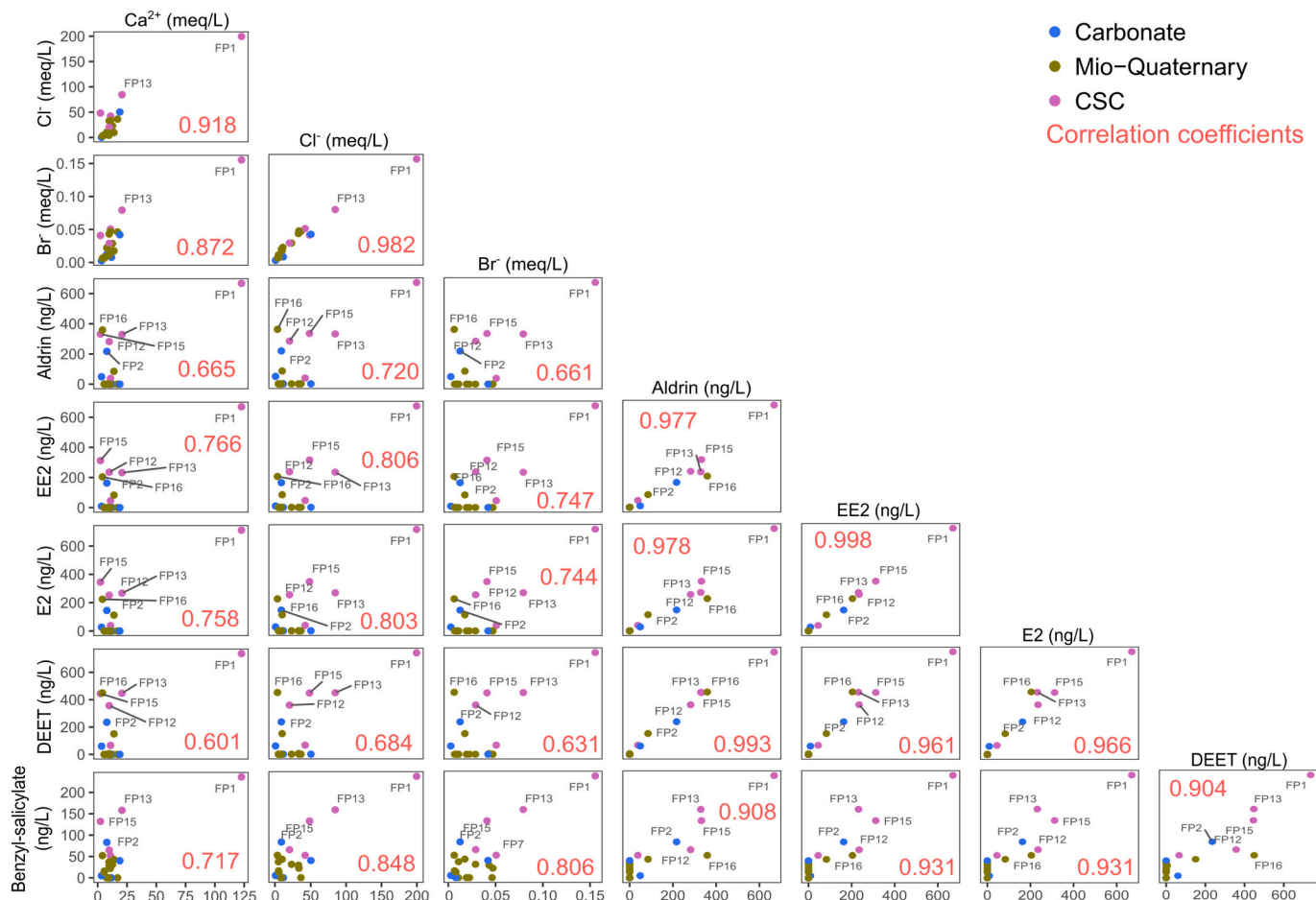


Fig. 7. Biplots of selected variables and correlation coefficients.

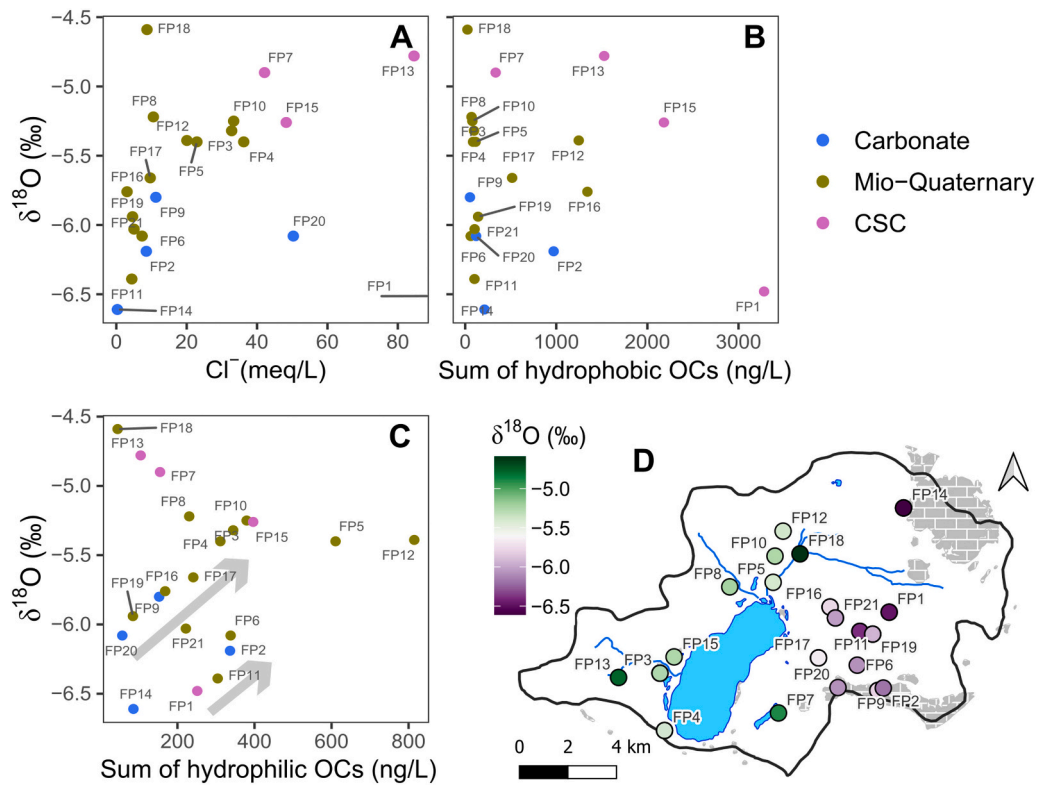


Fig. 8. Biplots showing the relationship between $\delta^{18}\text{O}$ and (A) Cl^- , (B) total concentration of more hydrophobic OCs ($\log K_{ow} < 2$; Table S6), and (C) total concentration of more hydrophilic OCs ($\log K_{ow} > 2$; Table S6) and (D) spatial distribution of $\delta^{18}\text{O}$. The concentration of Cl^- in FP1 is 200 meq/L.

Table 1

Table showing depths of sampling points and concentration (ng/L) of selected organic contaminants. Shaded cells aim to highlight the presence of contaminants in deep sampling points. '<LOD' means below the level of detection.

Point	Aquifer	Depth	Aldrin	EE2	E2	DEET	Benzyl salicylate
FP1	Reach and cut CSC	84.5	668	670	712	737	236
FP2	Carbonate	116	217	163	145	235	83
FP3	Mio-Quaternary	6.5	<LOD	<LOD	<LOD	5	29
FP4	Mio-Quaternary	7.7	<LOD	<LOD	<LOD	<LOD	<LOD
FP5	Mio-Quaternary	25	<LOD	<LOD	<LOD	<LOD	31
FP6	Mio-Quaternary	Unknown	<LOD	<LOD	<LOD	<LOD	<LOD
FP7	Reach and cut CSC	150	38	45	38	66	52
FP8	Mio-Quaternary	6.8	<LOD	<LOD	<LOD	<LOD	<LOD
FP9	Carbonate	Unknown	<LOD	<LOD	<LOD	<LOD	<LOD
FP10	Mio-Quaternary	7	<LOD	<LOD	<LOD	<LOD	22
FP11	Mio-Quaternary	42	<LOD	<LOD	<LOD	<LOD	37
FP12	Reach and cut CSC	120	282	235	253	357	65
FP13	Reach and cut CSC	89.9	329	232	267	447	158
FP14	Carbonate	150	49	9	27	60	5
FP15	Reach and cut CSC	164	579	437,5	491,5	709,5	125
FP16	Mio-Quaternary	Unknown	359	204	224	449	52
FP17	Mio-Quaternary	Unknown	85	83	112	150	43
FP18	Mio-Quaternary	10	<LOD	<LOD	<LOD	<LOD	<LOD
FP19	Mio-Quaternary	25	<LOD	<LOD	<LOD	<LOD	16
FP20	Carbonate	149	<LOD	<LOD	<LOD	<LOD	40
FP21	Mio-Quaternary	Unknown	<LOD	<LOD	<LOD	<LOD	13

biodegradation than aldrin (Jorgenson, 2001) but was not detected in this study. Thus, this deep and saline underground environment provided by the CSC formation can contribute to the preservation of pollutants, which would explain the occurrence of the forbidden aldrin in those sampling points and the accumulation of OCs.

The monitoring campaign was conducted during the recharge season (Fig. S4). Nonetheless, there is no significant correlation between OCs and parameters that can represent a washing process from the soil by rainfall (i.e., pH, TOC, Saturation Index of calcite; Fig. 6A) even though this has been observed to play an important role in the distribution of OCs in the hydrogeological media in other studies (Corada-Fernández et al., 2017; Luque-Espinar et al., 2015; Llamas et al., 2022; Llamas et al., 2023). The lack of evidence of this process in this study may be attributed to the complexity of the system.

4. Conclusions

A special scientific contribution has been made through the first extensive screening of organic contaminants (OCs) in groundwater from a unique environment: the hydrogeological system of the Fuente de Piedra basin. This system includes hypersaline groundwater flows and supports a RAMSAR lagoon within the endorheic basin.

OCs, including contaminants of emerging concern (e.g., pharmaceuticals and personal care products), were detected in all water samples. Nine out of 32 detected compounds were detected at concentrations higher than 100 ng/L. The banned pesticide aldrin was found at a maximum concentration of 668 ng/L.

Isotopic data suggest a re-concentration process of the more mobile compounds potentially due to irrigation return flows in the Mio-Quaternary detrital aquifer. This is relevant for water management, as this aquifer is being exploited for urban water supply.

OCs can be accumulating in the deep and saline underground environment where a karstic aquifer is enclosed by a clayey and salty matrix (Chaotic Sub-baetic Complex or CSC). This formation constitutes the basement of the unconfined detrital and carbonate aquifers of the basin. From a water management perspective, this might seem unimportant since water resources from hypersaline environments are generally unsuitable for most human uses. Nonetheless, this formation is not isolated and its OC content can be of concern since (i) there is an induced groundwater recharge from the CSC formation toward the carbonate aquifers, which are exploited for urban supply; (ii) groundwater in the FP endorheic basin, including that from the CSC, naturally converge toward a RAMSAR lagoon and (iii) the CSC aquifer discharges occurs not only locally (toward the lagoon) but also regionally through hypersaline springs in the adjacent Guadalhorce River basin. The water of this river is collected in a dam system and distributed for irrigation and urban supply. This finding underscores the importance of preventing the emission of anthropogenic organic chemicals into the environment, as remediation strategies can be difficult to implement once the contaminants have reached significant depths. Conducting thorough controls of practices like the application of manure, slurry, and biosolids to agricultural lands will be key.

This study highlights the need to study the presence of OCs in water resources from the hydrogeological perspective to be able to address the forthcoming EU environmental requirements.

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CRedit authorship contribution statement

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

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2024.177712>.

Data availability

Data will be made available on request.

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