Pesticide water variability and prioritization: The first steps towards improving water management strategies in irrigation hydro-agriculture areas

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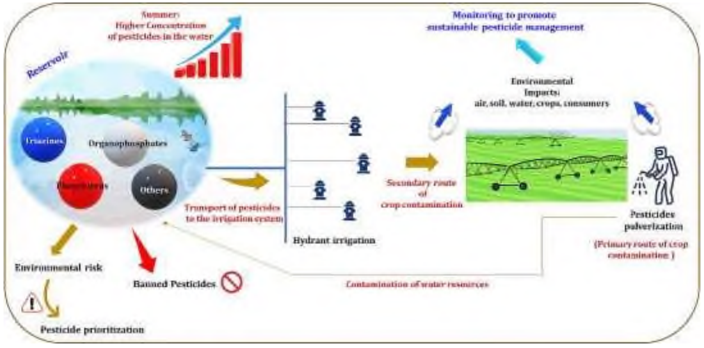
HIGHLIGHTS

- For the first time, understanding pesticide dynamics in irrigation system canals is proposed.
- Pesticides from reservoir to irrigation system; hydrants become a route of contamination.
- Climate change in Mediterranean connect with dynamic and environmental risk of pesticides
- Twelve pesticides presented high risk and were proposed to be added to the list of strict control.

GRAPHICAL ABSTRACT



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Abbreviations: EFMA, Alqueva Multiple Purpose Development; BHAS, Brinches-Enxoe Hydro-Agricultural System; LR, Lage Reservoir; MR, Montinhos Reservoir; RQ, risk quotient; MEC, measured environmental concentration; PNEC, predicted no-effect concentration; RS, ranking scores; FoE, frequency of exceedance; EoE, extent of exceedance.

ABSTRACT

The presence of pesticides in aquatic ecosystems poses significant risks to non-target organisms, necessitating monitoring and environmental risk assessment. This study aimed to evaluate the dynamics and environmental risk of pesticides in a hydro-agricultural area with intensive agricultural practices, in the Mediterranean region (South of Portugal). Seasonality and location influenced pesticide numbers and concentrations, with the highest levels observed during the dry season. Triazines, phenylureas, and organophosphates were the predominant pesticide contamination cycle Hydro-agricultural system pesticide classes, with terbuthylazine, bentazone, terbutryn, diazinon, and metolachlor exhibiting the highest detection frequencies (68 % to 72 %). Notably, 44 % of the quantified pesticides are no longer authorized in Portugal, with 33 % posing a high environmental risk. Some insecticides, including imidacloprid, methiocarb, and malathion, were occasionally detected at concentrations that posed high risks to the aquatic ecosystem (RQ ≥ 1). Irgarol, an algicide used in irrigation canals, presented a high risk in 91 % of the analysed samples.

The study's distribution profile of pesticides revealed a significant transportation of these compounds from reservoirs to irrigation hydrants, establishing them as a secondary source of crop and environmental contamination. Additionally, the assessment of spatial distribution and environmental risk allowed for the identification of specific pollutants in different locations, prioritizing them based on their ecotoxicological risk to aquatic ecosystems. These findings reinforce the importance of implementing management measures at the level of hydro-agricultural areas, helping to stop the cycle of pesticide contamination. Only this type of strategy will make it possible to protect water quality, biodiversity and the health of citizens, contributing to the European Union's objectives of improving the condition of freshwater bodies and promoting the sustainable use of pesticides.

1. Introduction

Currently, with the growth of the world population, the need to increase food production is a reality, constituting one of the greatest pressures for the maintenance of the balance of natural resources and ecosystem services (Tang et al., 2021). The agricultural sector faces this situation with the uncertainty of climate change and the appearance of new pests every day (Deutsch et al., 2018). Although the use of pesticides is important for maintaining agricultural productivity and crop health, when used in an unsustainable way, they can have negative impacts, promoting imbalance and compromising ecosystem services (McBratney et al., 2014). In fact, the environmental impact of these chemicals on nontarget species and on human health is an ongoing topic of concern. Indeed, chronic exposure to these substances has been linked to several health problems including immunosuppression, hormone disruption, reduced intelligence, reproductive abnormalities, cancer, infertility, malformation, chromosomal changes, DNA mutations, and oxidative stress (Bolognesi, 2003; Sabarwal et al., 2018; Yadav et al., 2015).

The contamination of water bodies by pesticides is influenced by several factors, such as chemical proprieties, agricultural practices, seasonality, hydrogeology, climate, biodegradation, and soil proprieties (Worrall and Kolpin, 2004; Yadav et al., 2015). During the environmental cycle, pesticides can undergo processes such as vaporization, adsorption, leaching, and washing, depending on their molecular characteristics and environmental conditions (Campanale et al., 2021).

Existing legislation in the European Union (EU) calls for the development of indicators to measure sustainable use of pesticides and monitoring their impact on human, animal, and ecosystem health. The Water Framework Directive (ECC, Directive 2000/60) is a legislative framework for protecting European surface waters, aiming to achieve a good ecological and chemical status by assessing their hydromorphological, biological, and chemical parameters (Arenas-Sanchez et al., 2019). Despite the EU's strict regulation of pesticides, excessive use is causing significant water quality issues in Europe due to various factors including infrastructural and technological, institutional and behavioural lock-ins (Hüesker and Lepenies, 2022). Infrastructural and technological lock-ins stem from historical land use patterns and EU agricultural policies that encourage large-scale production and industrialization of agriculture, resulting in the excessive use of pesticides. High production costs of pesticides, as well as a complex legal, scientific, and regulatory framework, also contribute to technological and infrastructural challenges. Institutional lock-ins arise from powerful political, social, and economic interests that exert influence over regulatory institutions, while behavioural lock-ins stem from cultural norms and ingrained social standards that lead to individual decisions that reinforce excessive pesticide use (Hüesker and Lepenies, 2022). In fact, all the gaps in pesticide application, use, and conservation guides, as well as in monitoring schemes in agricultural areas and in risk assessment after application, directly reflect the aforementioned such as structural and technological obstacles that end up perpetuating the trend of excessive pesticide use. This demonstrates the complexity of the challenge in seeking to reduce chemical contamination of water.

For improved resource efficiency in agricultural production, especially in regard to the use and quality of water and soil, it is crucial to conduct research aimed at understanding the behaviour of these contaminants in both abiotic and biotic compartments. Understanding the temporal variability of pesticides in irrigation water, their abiotic cycle and the environmental risks they pose is crucial for implementing sustainable management programs that protect ecosystems. Risk assessment has continuously evolved with new knowledge, such as the toxicity of relevant and non-relevant metabolites, cumulative toxicity, mixtures, and hypersensitive biological effects of very low concentrations of some pesticides (Vryzas et al., 2020). Nevertheless, to implement action plans for the sustainable use of pesticides, it is also necessary to determine which chemicals are more likely to occur in the environment and/or pose a risk to human health and to the environment (Daginnus et al., 2011). In this sense, the knowledge of pesticides dynamics and their prioritization are useful tools to complement risk assessment approaches as they can provide a more accurate risk forecast by categorizing the effects and/or occurrence of these substances. Pesticide prioritization methodologies have been developed to rank pesticides according to their environmental relevance and to facilitate ecotoxicological monitoring and testing programs focused on the priority molecules (Vryzas et al., 2020).

The Alentejo region in Portugal is a significant agricultural area, primarily producing cereals (wheat, maize, rye, barley, oats and rice), mediterranean crops (olive oil and wine), legumes, and potatoes (Faísca, 2019). Factors such as public investment in irrigation system, national and European Union (EU) policies, and financial strategies have led to the expansion of agriculture in the region (Silveira et al., 2018).

In that regard, the Alqueva Multiple Purpose Development (EFMA) has been a driving force behind the economic growth in Alentejo, enabling the intensification of agriculture and the expansion of irrigated crops (Palma et al., 2021). Besides, it provides water for various other purposes, such as public supply, industry, energy generation, and tourism (Palma et al., 2021; Tomaz et al., 2022). Nevertheless, the increase in irrigated areas also brought in an increase in pesticide use, which, in turn, can seep into reservoirs and decrease the quality of irrigation water. Recent studies in the Alqueva reservoir have indicated potential water quality issues due to the presence of pesticides, such as high environmental risk to ecosystems, elevated herbicide concentrations, and potential leaching and groundwater contamination (Palma et al., 2015, 2014, 2009).

The present study aimed to: (i) assess the cycle of pesticides in a smaller hydro-agricultural system of EFMA, analysing the concentration that occurred in the reservoirs and in the irrigation systems and those that were drained from the crops that could return to the reservoirs; (ii) prioritize the environmental risk of pesticide in the hydro-agricultural area (reservoir and irrigation system). This research focuses, for the first time, on the transfer of pesticides between different locations within an irrigation system, considering their respective sources of supply and their possible relationship with locally adopted agricultural practices. The analysis clarifies the temporal and local variability in the numbers and concentrations of investigated pesticides, as well as the occurrence of unauthorized substances in Portugal. The environmental risks associated with some of these pesticides can demonstrate the relevance of adopting monitoring programs adapted to specific hydro-agricultural areas, aiming to interrupt the cycle of pesticide contamination. The results obtained will support the implementation of more effective environmental management policies, contributing to the European Union's objectives of improving the status of freshwaters, and promoting the sustainable use of pesticides.

2. Material and methods

2.1. Study area

The study was conducted in the Brinches-Enxoe Hydro-Agricultural System (BHAS), which is located in the municipality of Serpa, in the district of Beja, Portugal. It is distributed along both sides of the Enxoe stream, between the reservoir of the same name and the Serpa reservoir, covering a benefited area of 5061 ha (EDIA, 2018). The BHAS belongs to the Ardila Irrigation Subsystem, which is part of the larger Alqueva Multipurpose Project (EFMA) in the Guadiana River Basin. It encompasses a secondary irrigation network of around 53 km, as well as 26.5 km of road network and 15 km of drainage network (Baptista and Gomes, 2012). The irrigated area of the BHAS is composed of three blocks, whose irrigation networks are pressurized through the pumping station located immediately downstream of the Lage reservoir or by a gravity network that starts at the Montinhos reservoir (EDIA, 2018). The BHAS's distribution network consists of a branched network of buried pipelines that are approximately 18.1 km long (NEMUS, 2008). The main agricultural activities in the Alqueva area comprise 84 % permanent crops (such as olive groves, almond trees, and vineyards) and 16 % annual crops (such as maize, rapeseed, barley, sunflowers, etc.). The olive grove is the crop that covers the largest area in EFMA, occupying approximately 65 % of the area (EDIA, 2022).

The region is characterized by a mesothermal Mediterranean climate (Faísca, 2019), type C in Koppen climate classification, subtype s (70 % of the precipitation in winter, and summer droughts) and sub-subtype a (hot Summers with average temperature >22 °C in the warmest month).

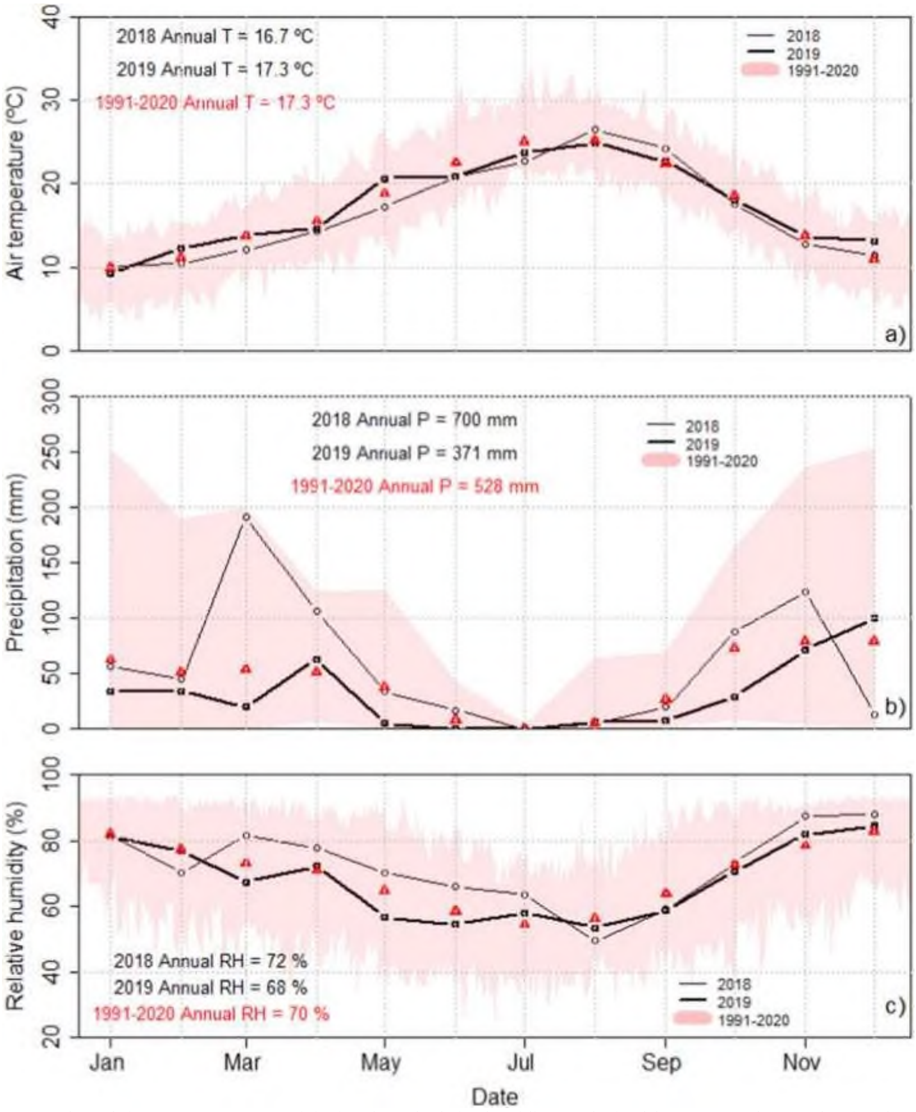

Fig. 1. Plots of air temperature (a), precipitation (b) and relative humidity (c) obtained from *E*-OBS dataset, showing the monthly variability of these variables during 2018 and 2019. The daily (monthly) variability during the climatological period 1991-2020 for air temperature and relative humidity (precipitation) is illustrated by the red shaded areas. The red triangles represent the climatological standard normal values.

Fig. 1 illustrates the daily variability of the 1991-2020 climatological period with respect to average air temperature, precipitation, and relative humidity (red shaded area), for Serpa municipality. The dataset (*E*-OBS) is based on observations from weather stations (Cornes et al., 2018**)** available from the Copernicus Climate Change Service (https://climate.copernicus.eu/; last accessed on 31 May 2023). The same dataset was also used to characterize the meteorological variables during 2018 and 2019, as illustrated in Fig. 1 (monthly values) and Table 1 (annual averages). The year 2018 had in general lower air temperatures and higher humidity and precipitation than 2019. The hydrology in the area is complex, with dry summers and rainfall during Autumn and Winter, leading to significant irrigation demands in the first case and concerns about the high sediment and nutrient loads that may be carried by the irrigation water. Additionally, controlling runoff and percolation can be difficult in regions where rainfall occurs after the end of the irrigation campaigns (Duarte and Mateos, 2022).

Generally, in Portugal during the years of the study, the most sold class of pesticides was fungicides (2018: 53.81 %; 2019: 58.43 %), followed by herbicides (2018: 24.05 %; 2019: 22.50 %), and insecticides (2018: 8.38 %; 2019: 8.29 %) (DGAV, 2021). Regarding the pesticides applied per region, there is a gap in the quantities used, particularly in hydro-agricultural systems. For the study area, the pesticide application information we have was provided by farmers detailing the agricultural practices used in each crop, which is displayed in Table S1. Therefore, Table S1 summarizes the pesticides applied for each crop during the 2018 and 2019 irrigation campaigns, as well as identifies the irrigation systems responsible for supplying each crop. The study was conducted as part of the GOFitoFarmGest Project for two consecutive years (2018 and 2019) with the goal of providing valuable information about the cycle of pesticides in the hydro-agricultural system and their potential impact on the aquatic ecosystems in areas of intensive agriculture.

2.2. Sampling

In this study, nine sampling sites were analysed: Lage reservoir (LR), where water samples were collected at two different points (LR1; LR2); five irrigation hydrants that receive water from the Lage reservoir (H1, H2, H3, H4, and H5); Montinhos Reservoir (MR) and the irrigation hydrant fed by it (H6) (see Fig. 2). For the irrigation of annual crops, such as sunflowers, corn, and clover, it was used a central pivot system, while a drip system was used to irrigate vineyards and olive groves. Water samples were taken in 2018 (July, October, and November) and 2019 (April, July, October, and November), during the irrigation campaign, to capture periods of pesticide application and crop growth phases. Furthermore, considering that one of the study objectives is the analysis of the variability of pesticides in the reservoir and irrigation system, samples must be collected when the hydrants are operational.

Samples of about 300 mL of water were collected in reservoirs at a depth of 50 cm with a Van Dorn bottle, and in irrigation hydrants after 1 or 2 min of running water, with the lowest possible pressure. The samples were transported to the laboratory in an insulated icebox, maintained at a temperature of 4 ◦C. The samples were stored in amber polyethylene terephthalate (PET) bottles, kept in the dark to prevent pesticide degradation, at —18 ◦C prior to analysis.

Table 1

Mean air temperature, accumulated precipitation and relative humidity obtained from E-OBS dataset (Cornes et al., 2018), for the periods indicated.

Period	Air temperature (°C)	Accumulated precipitation (mm)	Relative humidity (%)
2018	16.7	700	72
2019	17.3	371	68
1991-2020	17.3	528	70

2.3. LC-MS/MS analysis

A total of 51 target pesticides, representative of different chemical classes and modes of action (herbicides, insecticides, and fungicides), were explored. Chosen pesticides included EU priority substances, pesticides listed in the watch lists, pesticides commonly applied in Portugal, and some of their transformation products. In addition, this target group included 9 active substances among those used in the analysed crops, including all insecticides applied (deltamethrin, imidacloprid, acetamiprid, dimethoate, chlorpyrifos-methyl) and the herbicides used in greater number of applications (pendimethalin, metalachlor, terbuthylazine, fluroxypyr) (Table S1). The analysis of this group of pesticides is related to its historical evaluation process that has been taking place since 2006 in the region under study, where the analysis of temporal and spatial variability has allowed for more solid conclusions to be drawn. The targeted pesticides were analysed according to Barbieri et al. (2020) following a methodology based on liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). Briefly, water samples (5 mL) were centrifuged for 10 min at 3500 rpm and preconcentrated onto previously conditioned CHROspe cartridges (divinylbenzene polymer, 10 mm x 2 mm i.d., 25-35 µm particle size) (Axel Semrau GmbH & Co. KG, Srockhovel, Germany) by an automated on-line solid phase extraction (SPE) system Prospekt-2 (Spark Holland, Emmen, The Netherlands) connected in series with the LC-MS/MS instrument. After sample loading, the cartridges were washed with 1 mL of water and subsequently eluted onto the chromatographic column, a Purospher® STAR RP-18 (100 mm x 2 mm i.d., 5 µm particle size) (Merck, Darmstadt, Germany), with a mobile phase of acetonitrile and water. The LC-MS/MS system consisted of a 1525 binary HPLC pump connected with a TQD triple-quadrupole mass spectrometer equipped with an electrospray (ESI) interface (Waters, Milford, MA, USA) operated in both positive and negative ionization modes. MS/MS acquisition was performed in the selected reaction monitoring (SRM) mode, acquiring 2 SRM transition per analyte and 1 SRM per deuterated analog. The methodology was validated in terms of linearity, accuracy, precision, sensitivity, and matrix effects. Limits of detection (LODs) achieved for the target pesticides are reported in Table S2 in SM.

2.4. Environmental risk assessment

The aquatic risk of pesticides from BHAS was evaluated using the Risk Quotient (RQ) approach, with the aim of identifying the substances most dangerous for the aquatic ecosystem. The results were then used to create a list of priority pesticides. The Risk Quotient for each pesticide, RQi, was calculated as the ratio of the measured environmental concentration (MEC) to the lowest predicted no-effect concentration (PNEC) (RQi = MEC/PNEC). The worst-case scenario was evaluated by taking the highest concentration recorded for each pesticide as MEC (RQex).

The PNEC values were obtained from either the NORMAN Ecotoxicology Database (https://www.norman-network.com/nds/ecotox/; Dulio and Ohe, 2013) or the FOOTPRINT Pesticide Database (FOOTPRINT PPDB; Agriculture and Environmental Research Unit, 2013), which contained ecotoxicological data for three freshwater trophic levels (algae, crustacean, and fish). The PNEC values were adjusted using an assessment factor in accordance with the Technical Guidance Document on Risk Assessment provided by the European Commission (ECC, 2003) (see Table S2). The Risk Quotient (RQ) of a single pesticide was classified into four categories based on the method proposed by Sánchez-Bayo et al. (2002): No risk (RQ < 0.01), low risk (0.01 ≤ RQ < 0.1), moderate risk (0.1 ≤ RQ < 1), and high risk (RQ ≥ 1). The PNEC values (concentration of pesticides without observed toxic effect) used in the model are obtained from the most sensitive aquatic species among those analysed (in general, the species used are from three trophic levels: algae, crustaceans and fish), and were adjusted with an assessment factor, ensuring that the determined risk is representative for the aquatic ecosystem under study, over a period of time and under specific conditions.

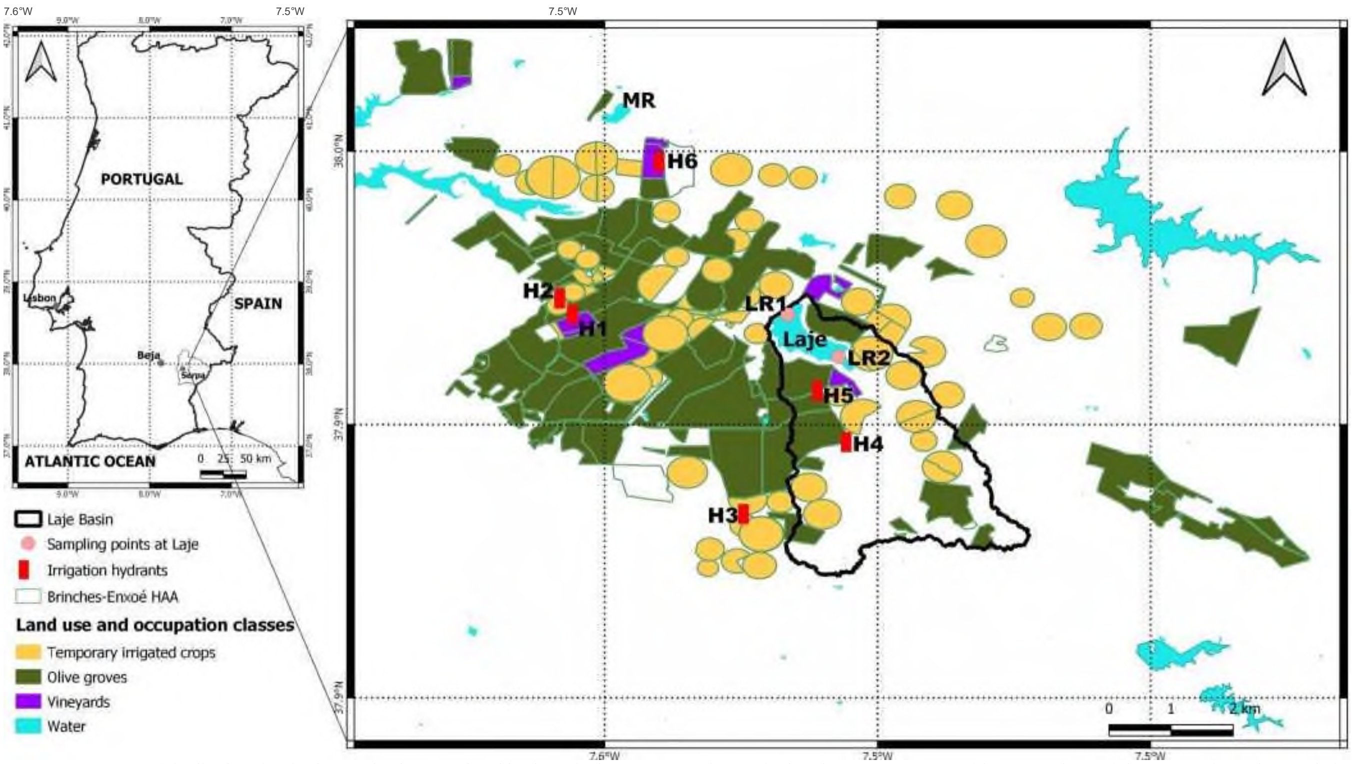

Fig. 2. a) Serpa municipality location in the South of Portugal and b) the Brinches-Enxoé Hydro-Agricultural System (BHAS) with Lage and Montinhos reservoirs and Lage drainage basin represented, as well as the irrigation hydrants and the sampling points. The colors represent Land Use and Occupation classes (COS2018) obtained from the Portuguese Directorate General for Territory (DGT —Direção-

Geral do Território).

In order to assess the extent of water pollution caused by pesticides and associated environmental risks across various sampling locations in the Guadiana Basin, an additive model was used to determine the site- specific risk (RQsite). This model involves adding up the individual RQi values of all compounds, assuming an additive action (AA) of the contaminants, as expressed in Eq. (1):

$$RQSite = \sum_{i=1}^{n} RQi \qquad (1)$$

Although this AA model may not be suitable for certain compounds with unknown behaviour in a mixture, it is widely recognized as a first tier approach (Backhaus and Faust, 2012; Palma et al., 2014).

2.5. Prioritization of pesticides based on their potential risk

The identification and prioritization of pesticides that may be added to the list of Specific Pollutants of Brinches-Enxoé hydro-agricultural irrigation system was done using the prioritization methodology of the NORMAN network, as outlined by Dulio and Ohe (2013). To determine the ranking of target pesticides in each sampling site, two risk indicators were employed: (i) Frequency of Exceedance (FoE) and (ii) Extent of Exceedance (EoE). Frequency of exceedance takes into account the spatial or temporal occurrence of a contaminant that is ecotoxicologically significant (Eq. (2)), while EoE considers the intensity of ecotoxicological risk (Eq. (3)).

$$FoE = \frac{\sum n}{N} \qquad (2)$$

where: n: number of samples with concentrations exceeding the lowest PNEC.

N: total number of samples

$$EoE = \frac{MEC95}{PNEC} \qquad (3)$$

MEC95: 95th percentile of measured concentrations for each pesticide. All concentration data above the LOQ are pooled and used to calculate a MEC_{95}.

PNEC: lowest predicted no-effect concentration.

The ranking score FoE value (RSFoE) ranges from 0 to 1 and is used directly in the calculation of the final ranking score (RS). The EoE value is ranked before being used in the RS calculation: EoE < 1 - RSEoE = 0; 10 ≥ EoE ≥ 1 - RSEoE = 0.1; 100 ≥ EoE > 10 - RSEoE = 0.2; 1000 ≥ EoE > 100 - RSEoE = 0.5; EoE > 1000 - RSEoE = 1.

The values of these two indicators are then summed to yield a final RS between 0 and 2 (Eq. (4)). Values of “non-detected” and “below the limit of determination” were treated as zeros.

$$RS = RSFoE + RSEoE \qquad (4)$$

2.6. Statistical analysis

Water data were assessed by descriptive statistics (median, range, and frequency of detection) and the seasonal and annual variations of the pesticides were analysed.

A correlation test was performed to evaluate possible associations among pesticides and temporal patterns. Hence, considering the number of samples (<50), and that most data failed the Shapiro-Wilk normality test, correlations between parameters were assessed using the Spearman's rank coefficients, as a non-parametric measure computed over ranked data, for a confidence level of $p < 0.05$.

All statistical analyses were performed with the STATISTICA 7.0 (Software™ Inc., PA, USA, 2004).

3. Results and discussion

3.1. Temporal distribution of pesticides in the hydro-agricultural irrigation area

The total concentrations and range for the detected pesticides are shown in Figs. 3 and 4. Among the quantified pesticides, the majority are herbicides followed by insecticides. Results of the temporal analysis revealed important differences in the total concentration and variability of pesticides between the two years, with 2019 being more polluted (with higher number and total concentrations of pesticides) than 2018. In 2018, a total of 22 pesticides were quantified in the irrigation water across the hydro-agricultural area, while in 2019 the number increased to 32. The study revealed a 49 % increase in total pesticide concentrations from 2018 to 2019 (3160 vs. 4713 ng/L). The highest total concentrations of pesticides were observed in July of both years (with a total concentration of 1652 and 2124 ng/L, respectively), as occurred in other studies carried out in central Spain (Arenas-Sánchez et al., 2019). In addition to extent of use, the intensification of evapotranspiration in the months of higher temperatures, lack of precipitation and lower humidity (typically between June and September in regions with a Mediterranean climate) may be one of the reasons found to justify these results. These meteorological conditions were more pronounced in 2019, being a slightly hotter and much drier year than 2018, as shown in Fig. 1. To note the high concentrations in the samplings taken at LR1 in July and October 2019, which could relate to the reduced rainfall in the period (48 mm), compared to the 164 mm in the same period of 2018, contributing to increased pressures in the water masses. Analysis of the correlation between the concentrations of pesticides detected in BHAS waters and climatic variables, such as temperature and precipitation

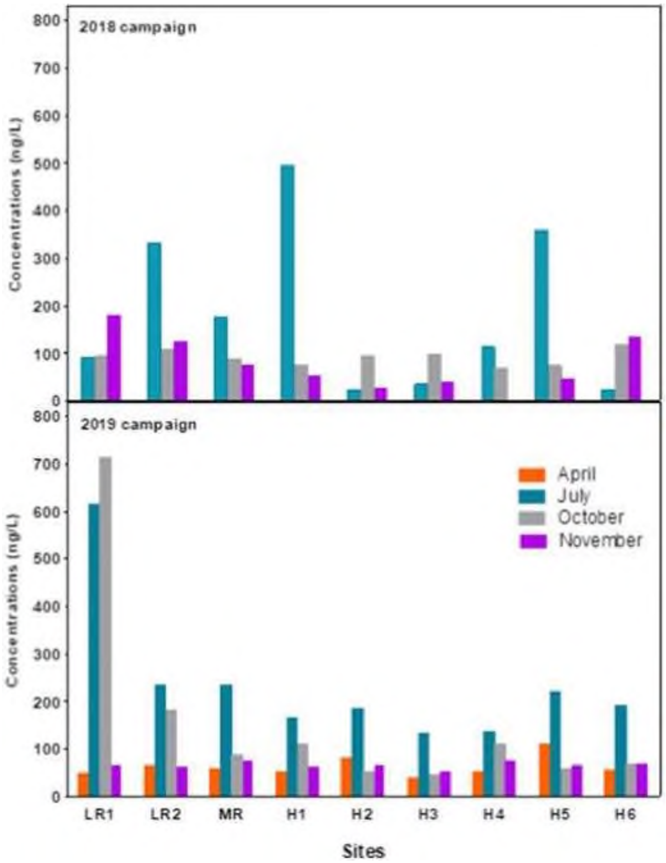

Fig. 3. Pesticide total concentrations for each sampling location in the sampling campaigns months during 2018 and 2019. Lage reservoir: LR1; LR2; MR: Montinhos reservoir; H1-6: irrigation hydrants.

(Table S3), revealed that pesticides like atrazine, diazinon, diuron, and metolachlor, exhibit a negative correlation with precipitation (R = —0.843; R = -0.554; R = -0.423; R = -0.439, respectively) and a positive correlation with temperature (see Table S3). This suggests that these pesticides concentrations are more likely to increase in the surface waters under conditions of lower precipitation and higher temperatures, possibly due to a greater evaporation rate. Another possible explanation is the runoff of some pesticides applied in previous years, which can accumulate in the soil if they show persistence times >100 days (DT_{50}_soil >100 d; Pesticide Properties Database, 2023). Which may be support by the observation of the positive correlation between the concentrations of imidacloprid, diflufenican, and chlortoluron and the increase in precipitation (R>0.8) (Table S3). Indeed, imidacloprid demonstrates persistence in the soil and a high leaching capacity (soil DT_{50} 191 d; GUS >2.8; Table S2). Furthermore, some of these substances may remain in the water compartment due to their high polarity, such as bentazone with log K_{ow} of — 0.46 and thifensulfuron-methyl with log K_{ow} of —1.65, and their stability in the aqueous phase with DT50 > 30 days. (e.g., bentazone, metolachlor, thiacloprid, atrazine, and simazine) (Table S2). A substantial risk of surface water contamination by these pesticides, particularly when they are transported in a dissolved state, has been reported (Dores and De-Lamonica-Freire, 2001). This risk is further exacerbated when rainfall occurs during the period of pesticide application (Dores and De-Lamonica-Freire, 2001).

During the 2018 campaign, the pesticides with the highest total concentrations were terbuthylazine (603 ng/L) and bentazone (443 ng/ L), while thifensulfuron-methyl obtained the highest punctual concentration of 306 ng/L. According to studies conducted in the Ebro River Delta (Catalonia, NE Spain) bentazone was the herbicide found in the highest concentrations (18 x 10^4 ng/L) and had the highest detection frequency (Barbieri et al., 2021). Further, a previous study conducted in the Guadiana Basin during 2017 and 2018, reported bentazone as the most prevalent herbicide among the group of acidic pesticides detected in the area (Palma et al., 2021).

Dimethoate was detected only one-time in 2018. It was applied in the crops, irrigated by H4 and H6, as a phytosanitary treatment in olive groves (deadline for use, in Portugal, had been set for 06/30/2020). Due to its high solubility and stability, this insecticide exhibits relatively high mobility (Table S2). According to de Souza et al. (2020), dimethoate is the insecticide most frequently detected in surface waters worldwide, with reported concentrations reaching as high as 61,200 ng/L in Costa Rica (Carazo-Rojas et al., 2018).

In the 2019 campaign, the same profile was observed, with terbuthylazine and bentazone having the highest total concentrations, with values of 1022.7 ng/L and 726.6 ng/L, respectively. Terbuthylazine (14.9 ng/L to 70.9 ng/L) and terbutryn (1.1 ng/L to 28.8 ng/L) were detected in all the analysed samples, while metolachlor (5.2 ng/L to 63.9 ng/L) was quantified in 94 % of the total samples. The high frequency of terbuthylazine has already been observed in other irrigation systems, within the Alqueva irrigation perimeter. The incidence of this substance could be attributed to its common usage in annual crops such as maize and sunflower (data from agriculture practices provided by the farmers (Table S1; and Palma et al., 2021). The herbicide metolachlor was one of the main compounds found in both annual irrigation campaigns, justified by its physico-chemical proprieties and intensive use in corn, soybean, potato, and cotton crops (Sun et al., 2019). Despite its high solubility in water, metolachlor is known to degrade slowly, with a high half-life in water (DT_{50} of 88 days; see Table S2), making it a frequent presence in surface waters. Other research studies have reported that metolachlor is one of the most frequently encountered compounds in water samples collected from agricultural areas (Barbieri et al., 2021; Battaglin et al., 2016; Glinski et al., 2018).

Among the pesticides analysed, alachlor, atrazine, chlorfenvinphos, diuron, isoproturon, quinoxyfen, terbutryn, and simazine are included in the list of priority substances for water policy, being their concentrations in surface waters at BHAS below the maximum allowable

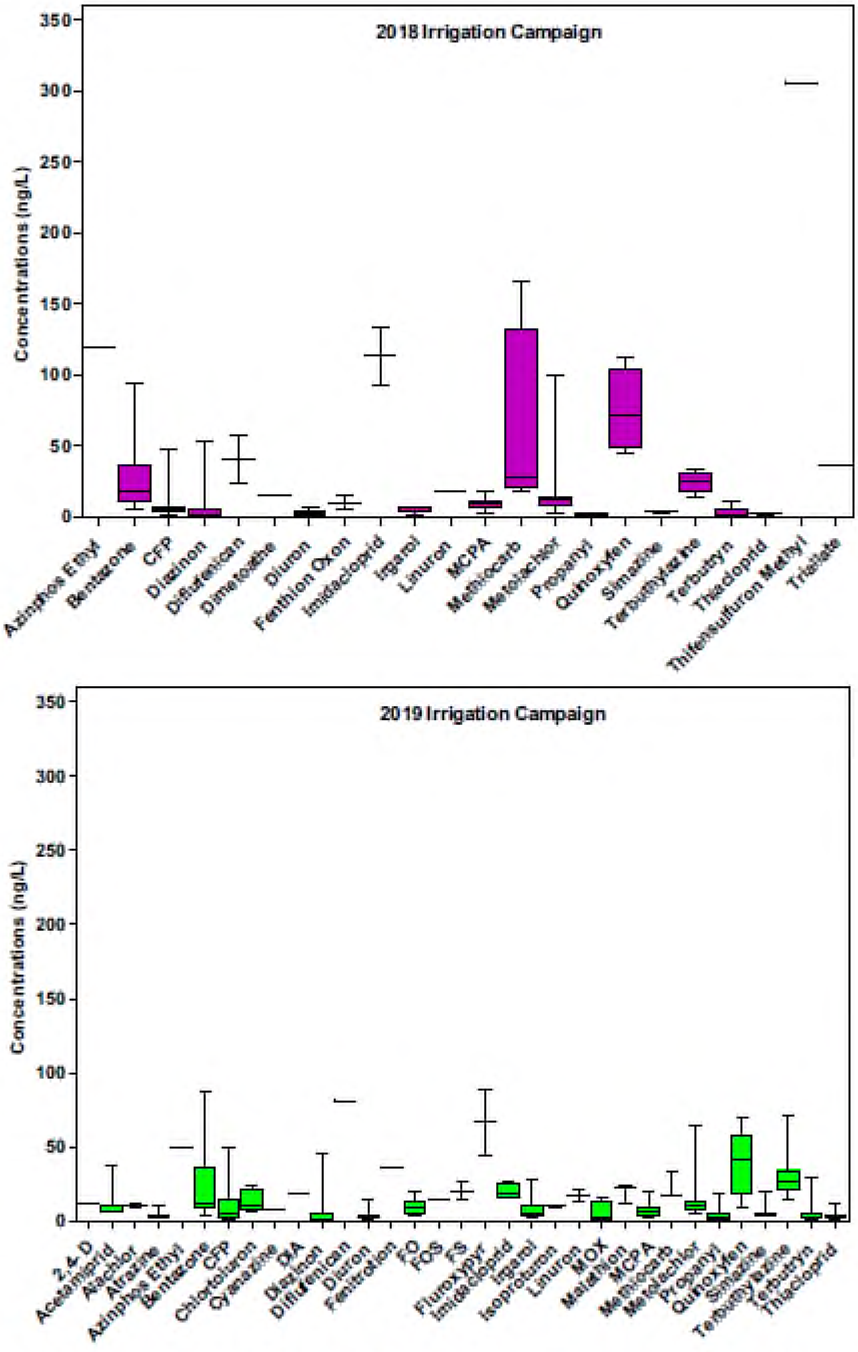

Fig. 4. Box and whisker plot of the concentration range for the quantified pesticides in the BHAS for both the 2018 and 2019 irrigation campaigns. A straight line inside the box indicates the median values; the box indicates the 25 % and 75 % cut of the values; the whiskers indicate the maximum and minimum.
CFP: Chlorfenvinphos; DIA: Desisopropyl atrazine; FO: Fenthion oxon; FOS: Fenthion Oxon Sulfoxide; FS: Fenthion Sulfoxide; MCPA: 2-methyl-4-chlorophenoxyacetic acid.

Environmental Quality Standards (EQS) levels, as outlined in Directive 2013/39/EU (ECC, 2013). On the contrary, irgarol (cybutryne) exceeded the limit values established by the directive, with concentrations of 22.8 ng/L and 28.4 ng/L observed at LR1 during the months of July and October 2019, respectively. In addition to the EQS values, other factors such as human exposure and the synergistic effect of multiple pesticides need to be considered when assessing the risk associated with a pesticide. Therefore, the presence of a chemical at levels below the EQS may still have adverse effects, especially with long-term exposure. The directive provides EQS for priority substances and advocates for monitoring substances of European concern.

Of the total quantified active substances, at least 44 % were no longer permitted for use in Portugal during the application period. These include alachlor, atrazine, azinphos ethyl, chlorfenvinphos (CFP), cyanazine, diazinon, diuron, fenitrothion, irgarol, isoproturon, malaoxon, malathion, propanyl, simazine, terbutryn, triallate (https://sifito.dgav.pt/; Fig. 5). The presence of these pesticides in several investigated locations may indicate their persistence in the environment due to previous applications, or in some cases they can still be applied to crops, for run out of stock, after their prohibition (Palma et al., 2021; Peris et al., 2022). This observation has already been reported in other studies that assessed the incidence of pesticides in the Alqueva reservoir and in some of its tributaries (Palma et al., 2021). Regarding some compounds such as ethyl azinphos (banned in Portugal since 2007), which have a high log Kow (>3), they can be adsorbed on suspended particles, accumulating in the soil and sediments, and are not expected to accumulate in the aqueous phase (Barbieri et al., 2021). Studies carried out in other European countries also reported the presence of this organophosphate insecticide in surface waters after its ban, suggesting that its presence would be attributed to its illegal application (Barbieri et al., 2021; Palma et al., 2021; Kapsi et al., 2019). The frequency of detection of these substances was higher in 2019, excepting for dimethoate. In 2018, among the banned pesticides, terbutryn, diazinon, and diuron were found in more than half of the water samples analysed (53 % to 73 %) (Fig. 4). The presence of the herbicide atrazine was always detected in low levels (1.8-11.3 ng/L), in at least 36 % of the water samples analysed in 2019. This pesticide, which has a symmetrical molecular structure and is hydrophobic, has been widely used on soybean and corn crops and is known for its persistence in aqueous solutions and moderately persistence in soil compartment (Table S2; de Souza et al., 2020).

3.2. Spatial distribution of pesticides in the hydro-agricultural irrigation area

Table 2 displays the total annual concentration measured for each pesticide at the respective sampling sites. In the Lage and Montinhos reservoirs, 18 and 13 pesticides were detected, respectively. Most of the pesticides found in the hydrants were detected in the reservoirs, but not all pesticides detected in the reservoirs were detected in the hydrants. The percentage of pesticides found in LR in 2018, that were also quantified in the respective hydrants ranged from 39 % to 61 %: H1 (61%, supplying maize, sunflower, and vineyard crops); H2 (39%, irrigated maize and sunflower crops); H3 (50%, irrigated sunflower and clover crops); H4 (44%, irrigated olive grove crops), and H5 (44%, irrigated maize, sunflower, and vineyard crops). Considering the Montinhos reservoir, 54 % of the pesticides detected in it were also quantified in H6, which irrigates vineyard and olive grove crops.

In 2019, 31 pesticides were quantified in LR, and 16 in MR. The percentage of pesticides transported from LR to their respective hydrants ranged from 35 % to 52 %, while from MR to H6, it was 94 %.

However, some pesticides were solely detected in certain hydrants: thifensulfuron methyl and linuron in H1, triallate in H4, and azinphos ethyl in H5 (2018), and imidacloprid (2019). The last one was found in irrigation hydrants H1, H2, H3, and H5, with concentrations ranging from 16.2 to 26.3 ng/L, only during the month of April. In H6, which receives water from MR, two additional pesticides (acetamiprid and fenthion oxon) were detected.

Considerable variations were also observed for the concentrations of pesticides quantified in the reservoirs and hydrants. During 2018, the highest overall pesticide concentrations were quantified at irrigation hydrants H1 (622.1 ng/L) and H5 (481.3 ng/L). The water of these hydrants presented higher pesticide concentrations compared to those detected at the Lage reservoir (LR1: 365.6 ng/L; LR2: 566.9 ng/L). Some of the pesticides that contributed to the elevated levels in hydrants, such as thifensulfuron-methyl, were not found in the Lage reservoir as already mentioned. On the other hand, the hydrant with the lowest occurrence of pesticides in the 2018 was H2 (total concentrations: 145.5 ng/L).

Otherwise, in 2019, the total concentration of pesticides in the Lage reservoir (LR1) was about 3-5 times higher than that in all other sites, reaching 1443.1 ng/L. In fact, among the pesticides and metabolites detected during this year, 10 were exclusively found in the Lage reservoir during July and/or October, including alachlor, azinphos ethyl, cyanazine, desisopropyl atrazine (DIA), diflufenican, fenitrothion,

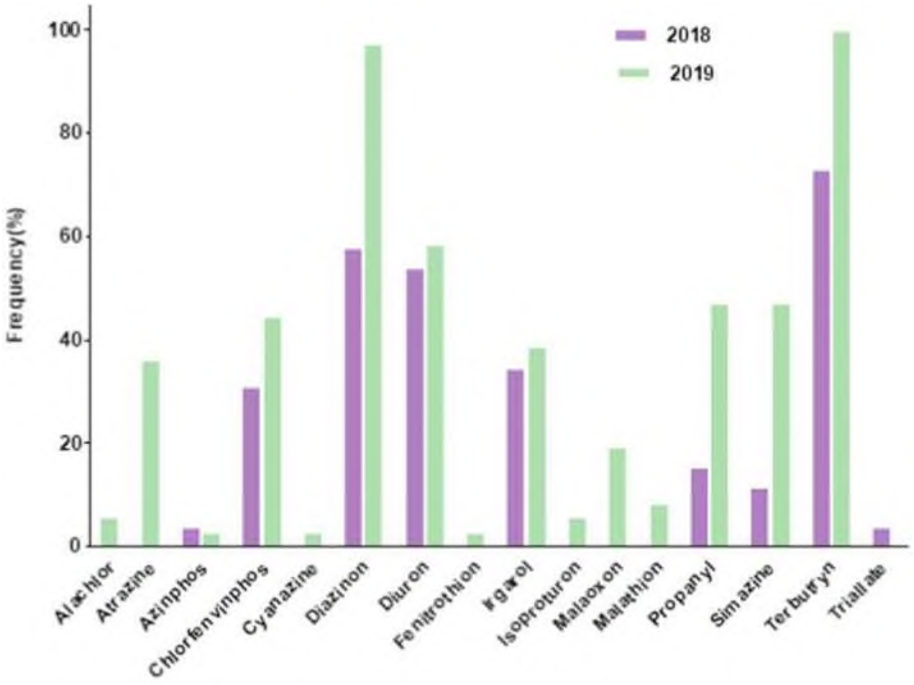

Fig. 5. Frequency of detection of banned pesticides in Portugal in water samples from BHAS.

Table 2

Total concentration (ng/L) of pesticides quantified in water samples, at each site, in the BHAS during two sequential years (2018-2019).

Pesticides	Sampling locations																	
	LR1		LR2		MR		H1		H2		H3		H4		H5		H6	
	2018	2019	2018	2019	2018	2019	2018	2019	2018	2019	2018	2019	2018	2019	2018	2019	2018	2019
2,4-D	n.d.	n.d.	n.d.	12.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetamiprid	n.d.	22.1	n.d.	13.1	n.d.	n.d.	n.d.	n.d.	n.d.	6.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	37.6
Alachlor	n.d.	21.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Atrazine	n.d.	24.3	n.d.	5.1	n.d.	2.7	n.d.	2.0	n.d.	2.0	n.d.	1.9	n.d.	2.5	n.d.	1.9	n.d.	6.4
Azinphos Ethyl	n.d.	49.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	119.3	n.d.	n.d.	n.d.
Bentazone	22.1	68.3	16.8	38	65.9	64.8	12.6	106.4	31.8	102.5	42.9	82.9	16	136.9	63.9	64.5	171	32.8
Chlorfenvinphos	6.6	85	8.1	30.9	8.9	17.9	n.d.	4.6	n.d.	3.7	5.7	1.8	n.d.	1.9	48.5	7.0	5.8	9.2
Chlortoluron	n.d.	12.8	n.d.	n.d.	n.d.	n.d.	n.d.	24.2	n.d.	9.1	n.d.	n.d.	n.d.	n.d.	n.d.	7.0	n.d.	n.d.
Cyanazine	n.d.	7.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DIA	n.d.	18.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Diazinon	8.2	79.8	6.6	33.9	11.6	19.9	8	6.6	0.5	5.5	5.2	5.7	5.8	5.3	55	8.6	6.1	10.9
Diflufenican	n.d.	81.3	57.8	n.d.	n.d.	n.d.	23.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dimetoathe	15.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Diuron	8.1	24.9	2.2	7.0	8.2	3.9	2.2	10.8	4.3	9.9	9.1	2.5	1.9	3.8	3.1	2.7	n.d.	6.8
Fenitrotion	n.d.	36.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fenthion Oxon	n.d.	32	15.4	18.3	5.2	n.d.	n.d.	4.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6.1
FOS	n.d.	14.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fenthion Sulfoxide	n.d.	47.4	n.d.	15.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fluroxypyr	n.d.	89.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Imidacloprid	133.3	n.d.	93.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Irgarol	9.0	53.7	12.5	20.0	10.7	11.1	6.7	3.7	n.d.	4.9	5.7	3.3	n.d.	3.0	n.d.	7.2	6.8	5.9
Isoproturon	n.d.	20.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Linuron	n.d.	34.5	n.d.	n.d.	n.d.	n.d.	18.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Malaoxon	n.d.	34	n.d.	9.1	n.d.	1.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.1
Malathion	n.d.	46.1	n.d.	n.d.	n.d.	12.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MCPA	18.8	30.4	21.6	11.9	27.5	15.3	5.7	4.4	12.1	9.5	9.6	9.3	n.d.	31.9	2.3	9.5	17.6	14.7
Methiocarb	18.4	49.9	166.2	n.d.	29.6	n.d.	27.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Metolachlor	36.6	46.5	8.5	30.1	36.1	37.6	118.2	29.1	14.8	38.4	32	32.7	13.3	28.3	n.d.	82.5	n.d.	35.9
Propanyl	1.9	37.9	2.5	14.6	3.8	10.3	n.d.	4.2	n.d.	3.6	n.d.	n.d.	n.d.	1.3	n.d.	2.9	n.d.	5.9
Quinoxyfen	n.d.	125.6	81.8	114.9	61.8	76.3	n.d.	11.8	n.d.	n.d.	n.d.	n.d.	44.4	n.d.	111.9	n.d.	n.d.	34.4
Simazine	n.d.	32.6	4.1	14.3	n.d.	8.1	3.9	8.3	n.d.	4.2	n.d.	3.8	2.5	5.4	n.d.	9.1	n.d.	8.2
Terbuthylazine	73.4	91.3	55.6	69.9	59.2	96.5	78.7	108.1	79.2	88.6	59.8	78.2	60.3	89	73.8	129.3	63	95.3
Terbutryn	12.2	51.9	10.9	21.1	13.6	15.7	10.4	9.9	2.8	9.9	3.6	7.8	1.7	9.2	3.5	12.1	7.8	10.4
Thiacloprid	1.4	25.0	2.6	10.7	2.4	5.2	n.d.	n.d.	n.d.	4.9	n.d.	n.d.	n.d.	6.7	n.d.	4.7	n.d.	5.3
Thifensulfuron Methyl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	306.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Triallate	n.d.	22.1	n.d.	13.1	n.d.	n.d.	n.d.	n.d.	n.d.	6.0	n.d.	n.d.	36.5	n.d.	n.d.	n.d.	n.d.	37.6

n.d.: not detected; DIA: Desisopropyl atrazine; FOS: Fenthion Oxon Sulfoxide; MCPA: 2-methyl-4-chlorophenoxyacetic acid.

fenthion oxon sulfoxide, fenthion sulfoxide, isoproturon, and linuron. Malaoxon and malathion were detected at both the LR and MR. The hydrants with the highest total pesticide concentrations were H5 with 460.9 ng/L, followed by H1 with 390.7 ng/L.

It is noteworthy that the surrounding areas of the reservoirs of the BHAS comprise other permanent and annual crops irrigated by H1 to H6. Consequently, these reservoirs also harbour pesticides originating from neighbouring crops. From these results it is possible to observe that the dynamics of pesticides in BHAS is influenced by the physical- chemical properties of these compounds and their interaction with the abiotic and biotic matrices, and also by the structural outline of the hydro-agricultural system. In relation to this last, for example, the distance between the hydrants and reservoirs can vary, and the water can flow through open or closed network of canals from the reservoir to the hydrant. Given the high solar radiation exposure in this region, there is a potential for pesticide degradation through photolysis, leading to a reduction in their half-life (Barceló and Hennion, 1997). Furthermore, contaminations can occur along the network of irrigation system canals. These conditions may explain the differences in concentration levels and the number and type of pesticides found in reservoirs and hydrants, as well as the variations among hydrants supplied by the same reservoir. These findings indicate that, in addition to primary contamination by pesticides, of abiotic compartments (soil, water and air) (El-Nahhal et al., 2017; Prosser et al., 2020) from spraying crops, irrigation water through hydrants can serve as a secondary source of contamination. This water may carry active substances different from those applied in each crop. On the other hand, pesticides from direct application and irrigation not only contaminate the crops but also the soil and water, creating a transport cycle of contamination with various environmental implications.

3.3. Environmental risk assessment

The RQ method was used to evaluate the environmental risk of pesticides quantified in the Brinches-Enxoé Hydro-Agricultural system. The study not only focuses on risk assessment in reservoirs, as a way of knowing the impact of pesticide concentrations on aquatic ecosystems, but also extends the methodology to analyse hydrants, aiming to understand the distribution and risk patterns throughout the irrigated system. Table S2 presents the respective PNEC values, and Fig. 6 presents the corresponding RQ values for the spatial and temporal distribution of each pesticide concentration. Thirty-three percent of the active substances detected in the BHAS were found in concentrations that pose environmental risk (RQ ≥ 1), particularly during the dry season. Most of the high-risk pesticides belong to the organophosphate class (azinphos ethyl, chlorfenvinphos, diazinon, fenitrothion, and malathion), neon- icotinoids (imidacloprid and thiacloprid), and triazine classes (terbutryn and irgarol). This type of analysis can predict some changes in the aquatic ecosystem, as the commitment of some species can cause, in the medium and long term, a disturbance in the ecosystem's balance. For example, insecticides were more toxic to crustaceans, the impact to some species of crustaceans can compromise the ecosystem with an increase in primary consumers such as algae, and a decrease in secondary consumers such as fish.

The Lage Reservoir (LR) presented a higher environmental risk for aquatic species compared to the Montinhos Reservoir (MR). This is consistent with the expectation that highly polluted sites coincide with those exhibiting the greatest environmental risk (Köck-Schulmeyer et al., 2021). The LR exhibited elevated risk for a total of 11 compounds, reaching a RQ of up to 246 for azinphos ethyl. Conversely, the MR showed a RQ up to 10 for malathion, with 5 pesticides posing an environmental risk. High risk was observed in 35 % of the samples in LR1, 10 % in LR2, and 11 % in MR (Fig. 6).

The algaecide irgarol, one of the most frequently detected substances, posed a high environmental risk, particularly in July, in all the 9 locations studied, in 91 % of the samples where it was quantified. Azinphos ethyl was the pesticide that presented the highest individual risk, with RQ values of 246 and 595, observed in LR1 in October 2019 and H5 in July 2018, respectively. Chlorfenvinphos and diazinon posed a risk to aquatic organisms in the reservoirs and in the H5 hydrant (with RQ values ranging from 1.01 to 4.99). Imidacloprid, methiocarb and malathion were occasionally detected, but always in concentrations that could pose a risk to aquatic ecosystems (with RQ values of 1.95-16, 1.69-16.62, and 10.17-19.5, respectively). Terbutryn and fenitrothion presented a high environmental risk in LR1_2019. Terbutryn presented a moderate risk in all the other samples where it was detected. The results showed that the most frequently detected herbicides, i.e. bentazone, metolachlor and terbuthylazine, occurred in concentrations that do not represent an environmental risk in this hydro-agricultural irrigation area. The pattern in the irrigation system showed that the majority of hydrants did not have pesticide concentrations that would pose a risk to aquatic species. The most problematic were H1 and H5, with an estimated hypothetical environmental risk incidence of 8 %. Thus, despite the transfer of pesticides from the reservoirs to the irrigation system, the concentrations reaching the hydrants were lower, thereby showing a reduction of the potential risk associated with pesticides along the irrigation system.

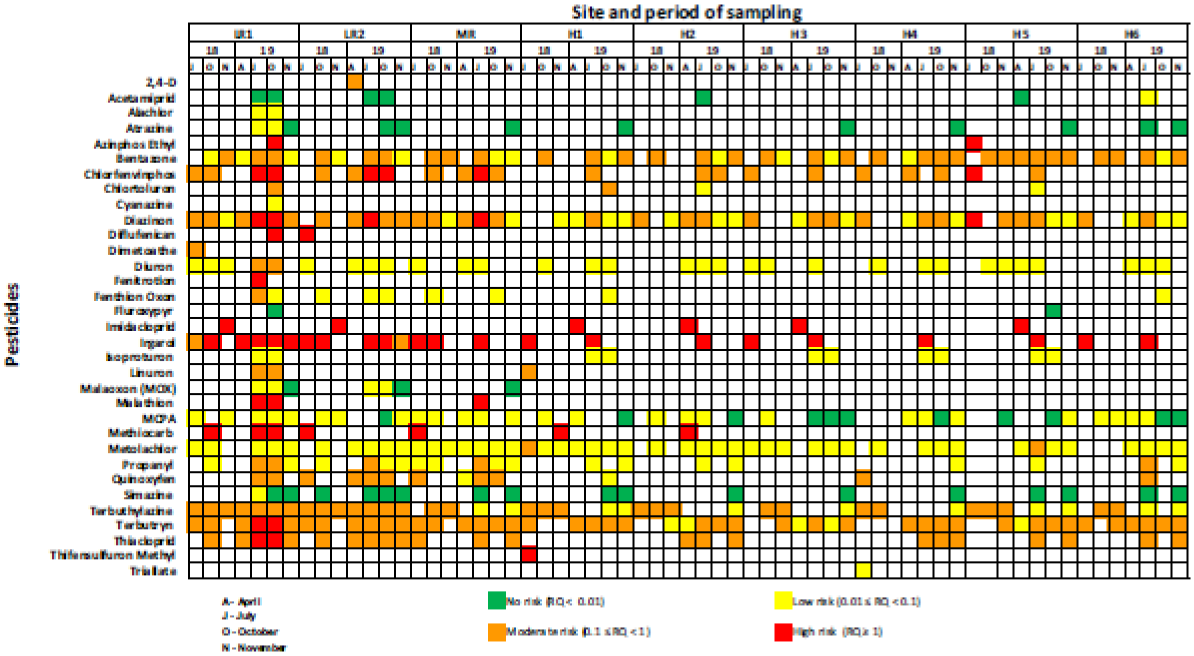

Fig. 6. Risk quotients for each pesticide at the nine sampling sites throughout seven campaigns carried out in the period 2018–2019.

3.4. Prioritization of pesticides

The identification and prioritization of pesticides for inclusion in the list of specific pollutants of BHAS was performed using the NORMAN methodology. Table 3 displays the prioritization of the pesticides based on the calculated ranking scores (RS) and the contribution of the corresponding FoE and EoE to them.

The extent of exceedance emerged as the dominant factor in the total score, reflecting the occurrence of several pesticides at concentrations far higher than their PNECs. This is the case of nine out of the twelve compounds surpassing the PNEC. Chlorfenvinphos showed similar contribution of EoE and FoE and the remaining two compounds (irgarol an terbutryn) were prioritized based on the frequency of exceedance.

Pesticides with higher RS scores signify the highest overall risk and should be given priority for regulatory action. Azinphos ethyl, followed by irgarol, obtained the highest RS scores (0.53 and 0.44, respectively), indicating a significant potential risk in terms of adverse effects and exposure. Methiocarb (0.31) and imidacloprid

(0.30) also displayed elevated RS. These values surpass those reported for the Guadiana Basin, where the herbicide bentazone scored the highest RS (0.26) (Palma et al., 2021). On the other hand, terbutryn obtained very low scores (0.03), indicating a relatively low risk in terms of adverse effects and exposure. Azinphos ethyl, diazinon, diflufican, irgarol, metiocarb, and thiacloprid have also been identified as priority hazardous substances in Mediterranean rivers (Köck-Schulmeyer et al., 2021).

Among the key compounds with a final score higher than 0, imidacloprid is widely used in soybean crops (Conte et al., 2022), while in the Guadiana Basin, it is frequently applied in horticultural practices (Palma et al., 2021). Irgarol, commonly used as an antifoulant in coastal areas with high boating activities, has been detected in harbors and marinas worldwide in recent decades (Fernández and Gardinali, 2016). Its proven toxicity and effects on aquatic life raise concerns about its ecological impact (Gittens et al., 2013), and its use is regulated under the European Union's biocide directive. Azinphos ethyl and methiocarb are prohibited for use in the pesticide category under Commission Delegated Regulation (EU) 2022/643 (Official Journal of the European Union, 2022). In Portugal, the usage deadline for methiocarb expired in April 2020. These findings emphasize the critical need for diligent monitoring and management strategies to mitigate the potential environmental risks associated with these pesticides in the BHAS and ensure the protection of the aquatic ecosystem in the agricultural area. In fact, to improve the sustainability of agricultural practices in this hydro-agricultural system, it could be proposed that pesticides of the same chemical class to those identified here as having high risk, but less toxic and hence safer for use as possible alternatives, could be for instance (according with the prioritization approach applied) dimethoate (PNEC 70 ng/L and RS 0) for replacement for azinphos ethyl (PNEC 0.2 ng/L and RS 0.53), terbuthylazine (PNEC 60 ng/L and RS 0) for replacement of irgarol in certain applications (PNEC 2.3 ng/L and RS 0.44), and acetamiprid (PNEC 3740 ng/L and RS 0) as substitute for imidacloprid (PNEC 8.3 ng/L and RS 0.30).

Table 3
Pesticides prioritization based on frequency and extent of exceedance scores (RSFoE; RSEoE), and total score priority ranking (RS).

	^{RS}EoE	^{RS}FoE	RS
Azinphos Ethyl	0.5	0.03	0.53
CFP	0.1	0.10	0.20
Diazinon	0.1	0.08	0.18
Diflufenican	0.1	0.03	0.13
Fenitrotion	0.1	0.02	0.12
Imidacloprid	0.2	0.10	0.30
Irgarol	0.1	0.34	0.44
Malathion	0.2	0.05	0.25
Metiocarb	0.2	0.11	0.31
Terbutryn	0.0	0.03	0.03
Thiacloprid	0.1	0.03	0.13
Thifensulfuron Methyl	0.1	0.02	0.12

4. Conclusion

Understanding the dynamics of pesticides in water resources is essential for farmers, researchers, companies, and management entities to develop intervention measures that promote better management of these chemicals, ultimately safeguarding the quality of water resources, soils, and agricultural products. The findings of this study highlight that the reservoirs supplying irrigation networks in agricultural systems are an important source of pesticide contamination. The distribution profile of pesticides revealed that most compounds found in irrigation hydrants are also present in the reservoirs that feed them. Out of all the pesticides quantified in the study, only four in 2018 and one in 2019 were not found in the Lage reservoir. A larger number of compounds and the highest total values of active substances were quantified mainly in 2019, with terbuthylazine, bentazone, and metolachlor being the pesticides with the highest total concentrations.

The results also highlight the transport of pesticides from the reservoir to the irrigation system, with the latter (via hydrants) being a secondary route of contamination of crops through irrigation water. Furthermore, the presence of certain substances in irrigation hydrants that were not detected in the reservoirs can indicate contamination along the network of irrigation system canals. Besides, pesticides detected are not applied by farmers to crops, showing the diversity of forms of water contamination that are present in the area.

Out of the 36 pesticides that were quantified, 12 were found to pose a high risk, with irgarol being particularly concerning due to its high frequency of detection at concentrations that can represent a risk for the aquatic environment. This substance has not been authorized for use in Portugal since 2013 and is also on the list of priority substances due to concerns about its toxicity and environmental impact.

The fact that 44 % of the detected pesticides are not authorized for use in Portugal and 25 % are on the list of priority substances in the water bodies of the hydro-agricultural system is worrying and highlights the need for active monitoring systems of these substances. Furthermore, analysing the potential sources of these unauthorized pesticides highlights the relevance of identifying their origin to implement appropriate preventive measures. Based on the results of the prioritization exercise, it is recommended that 12 pesticides be added to the BHAS list for strict control in the investigated irrigation perimeter. This monitoring will enable us to evaluate their potential negative impacts on water resources, soil, crops, and consumers, and promote sustainable pesticide management, resulting in increased efficiency and quality of water and agricultural crops. This effort is critical in ensuring the environmental, economic, and social sustainability of the agricultural sector in the future.

Indeed, the studies carried out in the areas of intensive agriculture research are highly relevant, since this type of agriculture must coexist with others that are less harmful to the environment, but also less productive. Therefore, to support food security and availability for all, it is necessary to improve good practices in this type of intensive agroecosystems. The global trend towards more sustainable agricultural practices surpasses conventional sustainable pest management. In fact, is essential that global rules encourage the development of other types of agriculture (less impactful) but must consider financial support to improve the environmental sustainability of intensive systems. By improving agricultural practices, we promote a reduction in the use of pesticides, a progress in the management of irrigation systems, with the advancement of water use efficiency, ensuring better soil health, aiming to protect water quality, with the enhancement of aquatic ecosystem.

Furthermore, in general, public policies to promote sustainability and protect aquatic environments are not temporally adjusted to research work. On the other hand, there is little monitoring work being carried out in these areas and consequently there is a lack of sufficiently robust databases to support possible regulatory changes. In this sense, it is crucial to promote an integrated approach for continuous collaboration between researchers, policymakers and relevant stakeholders, in order to enable more effective implementation of existing and future regulations.

Credit authorship contribution statement

Júnia Alves-Ferreira: Writing - original draft. **Manuel García Vara:** Investigation. **Adriana Catarino:** Investigation. **Inês Martins:** Investigation. **Clarisse Mourinha:** Investigation. **Marta Fabião:** Investigation. **Maria João Costa:** Writing - review & editing, Methodology. **Maria Vittoria Barbieri:** Investigation. **M. López de Alda:** Writing - review & editing, Supervision. **Patrícia Palma:** Writing - review & editing, Validation, Supervision, 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.

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.scitotenv.2024.170304.

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