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Occurrence and risk assessment of pesticides in a Mediterranean Basin with strong agricultural pressure (Guadiana Basin: Southern of Portugal)

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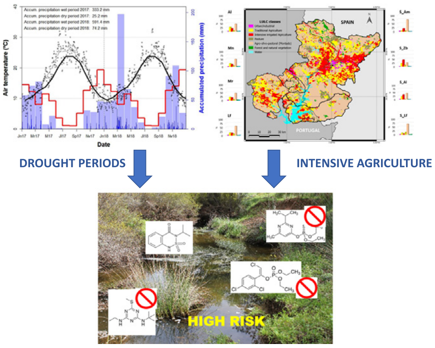
HIGHLIGHTS

- Drought enhanced the impact of pesticides in the ecosystems of Guadiana Basin.
- Quantified 23 European banned pesticides in the Guadiana Basin.
- Of the 38 pesticides detected, 32 may have induced risk to aquatic species.
- Bentazone, Terbutryn, Terbuthylazine, Chlorfenvinphos, Diazinon with high risk
- Greater risk in the streams of the Guadiana Basin than in the Alqueva reservoir

GRAPHICAL ABSTRACT



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ABSTRACT

The study aimed to assess the occurrence and the environmental risk of a group of 51 selected pesticides in the Guadiana Basin (a biodiversity hotspot, in the Mediterranean). The most abundant pesticides were bentazone and 2,4-D, while terbuthylazine together with terbutryn constituted the most ubiquitous pesticides. Eighteen out of the 38 pesticides detected are no longer approved in Europe, and 5 of them are included in the list of priority substances. The risk assessment showed that azinphos ethyl, diflufenican, irganol, imidacloprid, and oxadiazon occurred occasionally, but always in concentrations above their respective ecotoxicological threshold value. Contrary, bentazone, terbuthylazine, and terbutryn presented a high risk in most of the sampled locations and periods.

The site-specific risk assessment showed a spatial and temporal pattern, with a higher risk occurring mainly in intermittent streams, in the drought period. The presence of pesticides banned from the EU market since 2009 showed the importance of improving the monitoring process, to identify the main sources of pollution and the fate of these emerging compounds. The results showed the need of implementing actions to improve the sustainable use of pesticides in agricultural areas, working with farmers and management entities to reduce the contamination of aquatic ecosystems. Transboundary water governance is also required to solve potential transboundary contamination problems.

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1. Introduction

The “Green Revolution” changed the agriculture paradigm in the late 1960s. The introduction of selected seeds, the use of large quantities of fertilizers and pesticides, and the improvement of agriculture practices increased agricultural productivity and hence food production (Khush, 1999).

Cultivated land, with an extension of 15.3×10^6 km^2, has become the largest terrestrial biome in the world (Foley et al., 2011). Agriculture expansion resulted in a strong increase in pesticide production and use between 1955 and 2000 (Tilman et al., 2001). Pesticides still play a key role in the current agricultural model, as they generate substantial economic benefits. Their use reduces losses during the production process and promotes the corresponding decrease in product prices (Finizio and Villa, 2002).

Nowadays, there are almost 500 active substances approved in the European Union (EU), with sales of 360 million kg per year (Eurostat, 2018). Four countries, viz., France, Spain, Italy, and Germany, account for over two-thirds of the pesticide sales in the EU. While some European countries increased their pesticide sales during 2011–2018 ((Cyprus (+94%) and Austria (+53%)) other European countries made an effort to reduce them (−43% in Portugal and − 28% in Ireland) (Eurostat, 2018).

The massive use of pesticides becomes a serious threat as it may induce pest resistance (Heckel, 2012), leave pesticide traces in food commodities (levels above maximum residue limit (MRL) in 1.7% and 2.8% of the samples analyzed within the EU and Portugal, respectively, in 2015 (EFSA, 2017)), and unbalance the ecosystems (Llorens et al., 2020). To meet the world's future food security and sustainability needs, food production must grow substantially while, at the same time, agriculture's environmental footprint must shrink drastically (Foley et al., 2011). Actions such as the adoption of good agricultural practices that promote the decrease of pesticide use, the update of regulatory mechanisms, and the improved assessment of the occurrence and fate of pesticides in crops and watercourses can contribute to increment the environmental sustainability of agriculture.

The registration of new chemical substances in the European region is based on the REACH regulation (2006/1907/EC), while the protection of surface waters is based on the Water Framework Directive (2000/60/EC) and its daughter directives (Directives 2013/39/EC; 2008/105/EC; 2006/118/EC). Despite the current EU regulatory framework, studies continuously report pesticide contamination in the different environmental matrices worldwide (Barbieri et al., 2020a; Palma et al., 2015; Papadopoulou-Mourkidou et al., 2015; Ramírez-Morales et al., 2021; Silva et al., 2019). The levels found posed a potential risk for non-target organisms and overall, ecosystems (Čelić et al., 2021; Kandie et al., 2020; Llorens et al., 2020; Palma et al., 2009), which reveals the insufficiency of the regulatory and management procedures and the non-compliance of good agricultural practices (Köck-Schulmeyer et al., 2021; Ramírez-Morales et al., 2021).

Environmental monitoring is indeed an essential tool to increase the knowledge on pesticide pollution. It helps understand temporal and spatial pollution patterns at a regional scale, as well as the influence of stressors such as climate conditions and water scarcity on environmental concentrations (Ramírez-Morales et al., 2021; Sabater et al., 2018; Streissl et al., 2018). Furthermore, the combination of occurrence data with adverse effects allows the assessment of the potential impact of contamination in receiving aquatic ecosystems (Köck-Schulmeyer et al., 2021). Thus, the implementation of dynamic and integrative environmental risk assessment methodologies in post-registration real scenarios using advanced monitoring strategies (Altenburger et al., 2019) is a valuable tool to improve agricultural sustainability. This process can assist in the prioritization of pesticides in the environment, the adjustment of authorized doses, and the development of specific management actions.

In this context, the present study aimed at providing data on the occurrence of pesticides in the Guadiana River Basin (a Mediterranean Basin highly impacted by agriculture), and assessing the potential risk that the levels found may pose to freshwater organisms to obtain the ecotoxicological risk maps of the area. The study was conducted in hydrological years with accentuated meteorological differences, which allowed evaluating pesticide pollution patterns in drought and post-drought real scenarios, as well as the influence of climatic conditions in the associated environmental risk. The integration of the data obtained into maps of land use/land cover (LULC) also allowed identifying the crops that induce the greatest pressure in the basin. Moreover, the research also permitted to gain information about the Guadiana river basin specific pollutants (RBSP), a list of substances of concern that the water authorities must identify and control to ensure the good chemical and ecological status of the water bodies (Article 4 and Annex V; ECC, 2000). This set of results is very valuable to integrate the local farmers in the decision-making processes and raising concern on the adoption of good agricultural practice, allowing their integration and accountability in the decision-making processes.

Under such approach, the specific objectives addressed in the study were: (i) to identify the main pesticides occurring in the Guadiana River Basin; (ii) to analyze their spatial and temporal distribution; (iii) to assess the associated environmental risk; (iv) to obtain the pesticide risk areas and the major crops responsible for the risk observed, and (v) to prioritize pesticides for their eventual inclusion in the list of the Guadiana RBSP based on their occurrence and environmental risk.

2. Materials and methods

2.1. Study area and sampling sites characterization

The study was developed in the Portuguese territory of the Guadiana Basin, cataloged as one of the Portuguese areas most affected by water scarcity, reversed in part by the construction of the Alqueva Reservoir.

The Guadiana Basin is considered a biodiversity hotspot in the Mediterranean region. It is the most important national basin for the ichthyofauna conservation, with eleven species of freshwater fish, endemic to the Iberian Peninsula, four of them restricted to this basin, and among which are some endangered species, such as the Saramugo, the Boga, and the Shad of Guadiana. Further, it is the habitat to four native species of endangered bivalves, thirteen of the seventeen amphibian species existing in Portugal, and three species of turtles (www.icnf.pt). In addition, the Guadiana Basin is characterized by the presence of natural and semi-natural ecosystems included in the Habitat Directive (Directive 43/92/EU), such as *montado* (multifunctional agro-silvo-pastoral ecosystem, very typical at Southern Portugal, with varying densities of trees, mainly cork and/or holm oaks), temporary ponds, and intermittent rivers, to which high biodiversity is associated. The relief of the region is characterized by lowlands and smooth slopes, with dispersed mountains in the northwestern and southeastern areas that may reach up to 1000 m (see Fig. 1).

The Alqueva reservoir is a mover of Alentejo's economic development, as it allowed the intensification of agricultural activities and the implementation of large areas of irrigated crops. The reservoir, with a total storage capacity of 4150 hm^3, provides water for public supply, irrigation, industrial uses, energy production, and tourism. The global irrigation plan benefits a total area of 120,000 ha, of which about 70,000 ha were already in operation in 2017. The irrigation land increased to 93,000 ha during 2018 (www.edia.pt; Tomaz et al., 2020). This economic growth, based on the strengthening of the agricultural activity, may become a stress factor and an important diffuse source of pollution to the Guadiana Basin waters.

The study integrated the monitoring of eight freshwater sampling locations (coordinates provided in Table S1 as Supporting Information) at the Guadiana Basin during 2017 and 2018. Four of these sites were in the Alqueva reservoir: Álamos (Al), Mourão (Mr), Montante (Mn) and

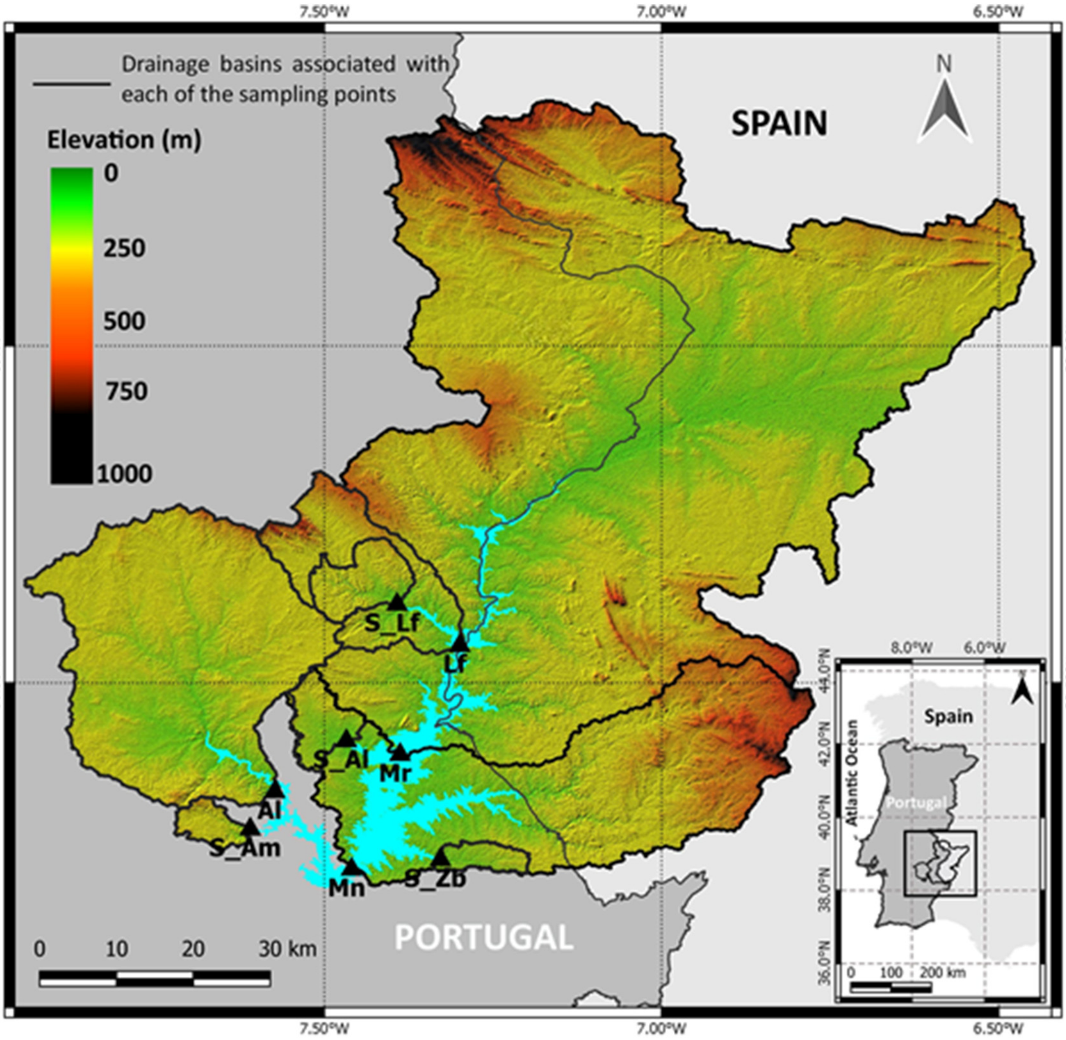

Fig. 1. Surface elevation map of the study region located in southwestern Iberia (bottom-right inset) illustrating the position of the sampling sites with the respective drainage basins.

Lucefécit (Lf). These sampling sites, with lentic conditions, have fixed platforms from where the samples were collected. These platforms also have meteorological devices installed to evaluate climate conditions. Montante and Mourão platforms are located in clear-cut surroundings and deep areas of the reservoir, with 60 m and 50 m depth, respectively; whilst Álamos and Lucefécit platforms are located in a forested surrounding and a 20 m depth area. The remaining four sampling points are located in Guadiana streams, tributaries to the Alqueva reservoir: Zebro drains into the reservoir near Montante platform (S_Zb); Álamos near Mourão platform (S_Al); Amieira near Álamos platform (S_Am); and Lucefécit near Lucefécit platform (S_Lf). The streams presented different hydrological regimes, characteristic of the Mediterranean region: (i) Amieira and Álamos are intermittent streams, drying to a series of disconnected pools part of the year (during the study this occurred in July and September in both years); (ii) Zebro presents an intermittent regime with water all year long but without flow during some periods (July, September, and November in 2017; and May, July, and September in 2018); and (iii) Lucefécit presents a perennial regime. A detailed description of the sampling locations can be found elsewhere (Palma et al., 2016; Palma et al., 2020a, 2020b; Palma et al., 2021). The region considered in this study matches the overlap of the drainage basins associated with each sampling site yielding an area of about 8660 km^2, and roughly corresponds to the northern half of the drainage basin of the Guadiana River section in Portugal (Palma et al., 2020a, 2020b). Fig. 1 displays the sampling locations with their respective drainage basins. Mn is the sampling location associated with the most extensive drainage basin. It drains an area of 7330.2 km^2, and includes Mr, Lf, S_Zb, S_Al, and S_Lf drainage basins. In turn, Mr comprises an area of 5910.3 km^2 and includes Lf and S_Lf drainage basins, whereas Lf (424.8 km^2) includes S_Lf (117.1 km^2). The drainage basins of Al (1279.0 km^2) and S_Am (50.8 km^2) are not overlapped by other basins.

Pesticides were analyzed during 12 sampling campaigns, performed bi-monthly from January 2017 to November 2018. The wet period included the months of November, January, and March, and the dry period included the months of May, July, and September. These periods were defined by the Environmental Portuguese Agency for the Alentejo region (ARHAlentejo, 2011). In general, when the streams were in the dry phase, the collection was performed in isolated pools upstream of the regular sampling sites. During the study period, a total of 96 water samples (300 mL) were collected at a depth of 50 cm, transported to the laboratory at 4 °C, and stored in amber polyethylene terephthalate (PET) bottles in the dark at −18 °C until analysis.

2.2. Meteorological conditions and land use/ land cover (LULC) analysis

The years under analysis in this study are 2017 and 2018, which from the meteorological point of view presented very different conditions in continental Portugal, as reported by the national authority - Portuguese Institute for Sea and Atmosphere (IPMA; www.ipma.pt; last accessed 19/03/2021). The year 2017 was warm and dry compared to the climatological normal for the period 1971–2000, with an average temperature 1 °C higher and about 40% less precipitation. This year was indeed the second warmest and the third driest year in the country since 1931. In contrast, 2018 was very similar to the 1971–2000 climatological normal in terms of temperature and precipitation values. The meteorological drought that started in 2017 extended until the beginning of March 2018, which was the second rainiest March in the country since 1931.

As illustrated in Fig. 2, the year 2017 presented much lower monthly precipitation values (light blue bars) than the 1971–2000 climatological normal for the region (solid red line), and higher monthly air temperatures between April and October. The monthly temperature and precipitation values measured in 2018 were close to the monthly values of the climatological normal for this region. The monthly temperature was above the normal in August and September and while extremely high precipitation was recorded in March, December was drier compared to the normal monthly precipitation average. The accumulated precipitation values in the four periods considered in this study were also calculated (Fig. 2).

The LULC characterization was obtained from the 2018 CORINE Land Cover (CLC), a Pan-European inventory available from Copernicus Land Monitoring Service (https://land.copernicus.eu/). The CLC database uses high spatial resolution satellite imagery to classify LULC in 44 distinct classes, with a minimum width of 100 m for linear phenomena and an area of 25 ha for the smallest mapping unit (Kosztra et al., 2017). The inventory distinguishes 11 classes for agricultural areas, which were grouped into 4 classes for the study purposes as shown in Table S2: Traditional Agriculture, Intensive Irrigated Agriculture, Pasture, and Agro-silvopastoral system (Montado). The other classes considered in the study were: Urban/Industrial, which included all Artificial Surfaces in CLC, Forest and natural vegetation, and Water.

The drainage basins corresponding to each of the sampling points (represented in Fig. 1) were obtained from Shuttle Radar Topography Mission (SRTM) elevation data with 1 arcsecond (30 m) resolution, as described in Palma et al. (2021). The LULC map of the areas corresponding to each class inside each of the drainage basins (see Fig. 1) is presented in Section 3.1.

2.3. Analysis of pesticides

A total of 51 target pesticides, representative of different chemical classes and modes of action, were investigated (Table S3). Selected pesticides included EU priority substances, pesticides listed in the watch lists, pesticides commonly applied in Spain and Portugal, and some of their transformation products. Their analysis in the water samples collected was performed with a method based on online solid-phase extraction-liquid chromatography-tandem mass spectrometry (SPE-LC-MS/MS) as described in Barbieri et al. (2020a, 2020b). Briefly, samples are fortified with a mixture of 45 isotopically labeled pesticides for quantification purposes and centrifuged to remove suspended particles. Thereafter, the samples (5 mL), along with the aqueous calibration solutions, quality controls, and blanks, are SPE-extracted in a Prospekt-2 system (Spark Holland, Emmen, The Netherlands) using disposable CHROspe Polymer DVB (divinylbenzene polymer, 10 mm × 2 mm i.d., 25–35 μm particle size) cartridges (Axel Semrau GmbH & Co. KG, Srockhövel, Germany). The retained analytes are then released to the chromatographic column (a Purospher® STAR RP-18 end-capped column, 100 mm × 2 mm i.d., 5 μm particle size, Merck, Darmstadt, Germany) with a mobile phase consisting of acetonitrile and water delivered by a 1525 binary HPLC pump (Waters, Milford, MA, USA). Their MS/MS analysis is performed with a TQD triple-quadrupole mass spectrometer (Waters) equipped with an electrospray (ESI) interface. Acquisition of the 51 target pesticides is done in the selected reaction monitoring (SRM) mode, and alternating positive (43 analytes) and negative (8 analytes) ionization in a single analytical run. Further details on the method and its performance characteristics can be found in Barbieri et al. (2020a, 2020b). Method limits of detection (LODs) and determination (LODets) in surface water are in the range of 0.3–19 ng L^{-1} and 0.8–40 ng L^{-1}, respectively, for the majority of the target compounds (86%) (Table S3).

2.4. Environmental risk assessment

The risk quotient approach (RQ) was applied to identify the pesticides that may induce the major aquatic risk in the Guadiana Basin. The resulting information was used to elaborate the list of RBSP and the risk maps of the area. The risk quotient of a single pesticide (RQi) was calculated as the ratio between the pesticide measured environmental concentration (MEC) and its lowest predicted no-effect concentration (PNEC) (RQi = MEC/PNEC). The maximum concentration measured for each pesticide was used as MEC to assess the worst-case scenario (RQex) (Palma et al., 2014a). PNEC values were derived from: (i) the NORMAN Ecotoxicology Database (https://www.norman-network.com/nds/ecotox/; Dulio and Ohe, 2013); or (ii) ecotoxicological results reported for three freshwater trophic levels (algae, crustacean, fish) in the FOOTPRINT Pesticide Database (FOOTPRINT PPDB; AERU, 2013), adjusted by an assessment factor (AF), according to the Technical Guidance Document on Risk Assessment of the European Commission (ECC, 2003) (see Table S3).

According to Sanchez-Bayo and Baskaran (2002), the RQi was classified into four groups: No risk: RQ < 0.01; low risk: 0.01 ≤ RQ < 0.1; moderate risk: 0.1 ≤ RQ < 1; and high risk: RQ ≥ 1.

To obtain a broad analysis of water pollution by pesticides and the environmental risk associated with each sampling location of the Guadiana Basin, the site-specific risk (RQ*site*) was determined using an additive model (sum up of the RQi's of all compounds), which assumes an additive action (AA) of the contaminants, following the Eq. (1):

$$RQSite = \sum_{i=1}^{n} RQi \tag{1}$$

Even though not strictly applicable to many compounds with unknown behavior in a mixture, the AA model is generally accepted as a first-tier approach (Backhaus and Faust, 2012; Palma et al., 2014a).

The risk map of the area for each investigated year was obtained using the RQsite calculated at each sampling site (average of the six sampling campaigns). Spatial interpolation was done with the Inverse Distance Weighted interpolation method. This spatial analysis method assumes that the risks that are closer to each other are more similar than those that are more distant. Consequently, for a specific location, the risk values of the locations around will contribute with a greater

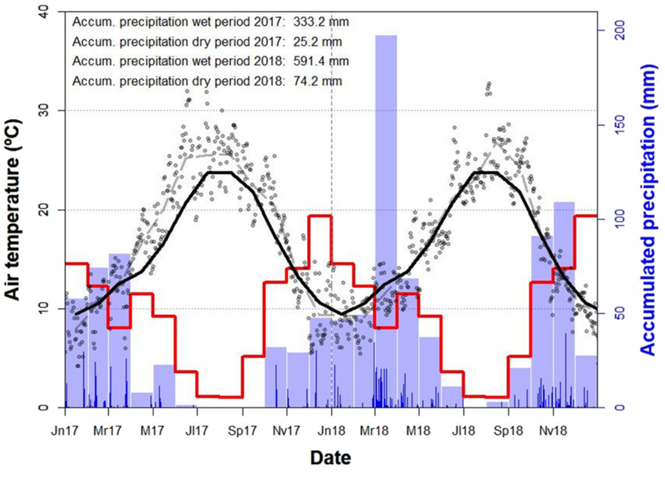

Fig. 2. Daily (grey circles) and monthly (grey dashed line) air temperature values and daily (dark blue bars) and monthly (light blue bars) accumulated precipitation measured in the region during 2017 and 2018. The solid black and red lines represent the 1971–2000 climatological normal for mean temperature and precipitation, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

weight to the risk prediction than the risk values of more distant locations.

2.5. Prioritization of pesticides based on their potential risk

The pesticides that could be included in the Guadiana RBSPs list were identified and prioritized following the NORMAN network prioritization methodology (Dulio and Ohe, 2013). Target pesticides detected in each sampling site were ranked using two risk indicators: (i) Frequency of Exceedance (FoE) and ii) Extent of Exceedance. The FoE considers the temporal or spatial occurrence of a contaminant with an ecotoxicological effect associated (Eq. (2)); while EoE ponders the intensity of the ecotoxicological risk, following the equation (Eq. (3)).

$$FoE = \frac{\sum n}{N} \tag{2}$$

n: number of samples with concentrations exceeding the lowest PNECN: number of total samples

$$EoE = \frac{MEC95}{PNEC} \tag{3}$$

MEC_{95}: 95th percentile of the measured concentrations for each pesticidePNEC: lowest predicted no effect concentration

The FoE value (RS_{FoE}) is comprised between 0 and 1 and is directly applied in the final ranking score (RS) calculation. In the case of the EoE, the value obtained is ranked as follows prior to their use in the RS calculation: $EoE < 1$ - $RS_{EoE} = 0$; $10 \geq EoE \geq 1$ - $RS_{EoE} = 0.1$; $100 \geq EoE > 10$ - $RS_{EoE} = 0.2$; $1000 \geq EoE > 100$ - $RS_{EoE} = 0.5$; $EoE > 1000$ - $RS_{EoE} = 1$.

The values of each of these two indicators are subsequently added to yield a final RS between 0 and 2 (Eq. (4)). For calculation purposes, "non detected" values and values "below the limit of determination" were treated as zeros.

$$RS = RS_{FoE} + RS_{EoE} \tag{4}$$

3. Results and discussion

3.1. Land use/ land cover (LULC) analysis

Fig. 3 shows the distribution in the study area of the seven LULC classes distinguished in this work.

The predominant class in most of the drainage basins is the Agro-silvo-pastoral (Montado), a particular ecosystem that only exists in the Mediterranean, especially in the southern Iberian Peninsula. Traditional Agriculture is the second most frequent class in five of the drainage basins (Al, Mn, Mr, Lf, and S_Lf), followed by the Intensive irrigated Agriculture class. Pasture class represents less than 10% of the area in all basins except for S_Lf (15%). The classes Urban/Industrial, Forest and natural vegetation, and Water hardly are expressed in all basins. Intensive Irrigated Agriculture, the class mostly correlated with the highest rates of pesticide application, covers an area of 1444.2 km^2, corresponding to 16.7% of the region. This was the predominant class in S_Zb (43%) and the second most frequent in S_Am (18.1%) and S_Al (33.1%).

Fig. S1 shows the map of the CLC Agricultural class distribution in the drainage basins, as well as the bar plots indicating the percentages of each CLC subclass included in the Intensive Irrigated Agriculture class used in this work (Table S2). In S_Zb basin, where Intensive Irrigated Agriculture is predominant, the main crop is olive groves (91.4%). This is also the major land cover within the Intensive Irrigated Agriculture class in S_Am (96.5%), and together with vineyards in S_Al (43.6% olive groves and 55% vineyards). In the remaining drainage basins (Al, Mn, Mr, Lf, and S_Lf), there is not a predominant CLC subclass, being most of their land cover shared by Permanently irrigated arable land, Vineyards, and Olive groves.

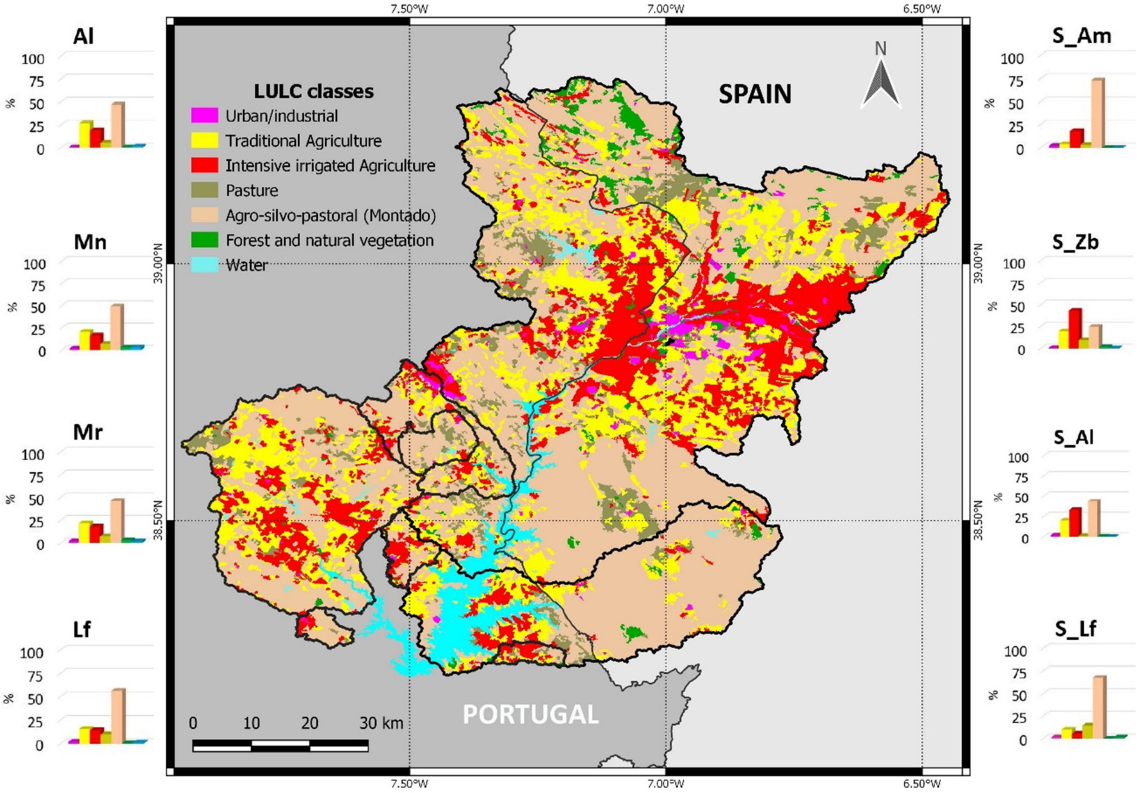

Fig. 3. Map of the LULC class distribution in the region of study and bar plots of the class percentages in each of the drainage basins. The seven classes are represented by the colors indicated in the legend. (For interpretation of the references to color in this figure legend, the reader is referred to the online version of this chapter.)

3.2. Occurrence of pesticides in the surface waters

Fig. 4 displays the total concentrations of pesticides quantified (a), with the corresponding distribution by classes (b), in each location and year (2017: drought year; 2018: pos-drought year). The results presented high spatial and temporal pesticide variability (Fig. 4a), showing no linkage among locations, and pointing out LULC and climate conditions as the most important factors for pesticide distribution. Spatial analysis showed overall higher concentrations of total pesticides in all Guadiana streams (4834 ng L^{-1} in S_Al, 5278 ng L^{-1} in S_Lf, and 6054 ng L^{-1} in S_Zb) except S_Am (158 ng L^{-1}), than in the reservoir. The low occurrence of pesticides in the Amieira (S_Am) may be justified by the low percentage of crops around the stream (22% of the land cover corresponding to traditional and intensive irrigated agriculture activities) and the high percentage of the agro-silvo-pastoral class (73%), which can also act as a buffer to the potential contamination generated in the crops (Palma et al., 2020a, 2020b).

The most contaminated area in the reservoir was Lucefécit (Lf) with a total pesticide concentration of 6931 ng L^{-1} in 2017. This location, however, has the lowest percentage of agricultural activities (traditional and intensive) in its drainage basin (30%), hence the occurrence of pesticides may be related to the steeper relief of the drainage basin that favors the runoff (Fig. 1). In contrast, Álamos (Al) was the location with the lowest occurrence of pesticides (total concentration: 630 ng L^{-1}), despite having 46% of its land covered by agricultural activities. This finding could be explained by the fact that this basin is extremely flat and thus, the runoff is hampered (Fig. 1). The results showed a spatial pesticide contamination pattern similar to that reported in previous studies, with the most contaminated areas occurring always in the northern part of the reservoir (Palma et al., 2009, 2014b).

Streams have been reported elsewhere as a source of nutrients and organic matter in the reservoir (Palma et al., 2020a, 2020b). However, the results obtained in this study did not support this hypothesis for pesticide contamination in the reservoir.

The temporal analysis revealed a marked difference between the two investigated years in terms of the pesticide contamination pattern, being 2017 considerably more contaminated than 2018 in all sites except S_Zb. As reported before, 2017 was classified as a drought year, extremely hot and dry. In general, in this year, the occurrence of pesticides in the waters was mainly observed between January and March, the period of rainy events (Tomaz et al., 2020).

Fig. 4b shows that the acidic class was dominant in the Guadiana Basin (44 to 88% contribution to the total pesticide concentrations), with bentazone as the most abundant herbicide in the group (63% of

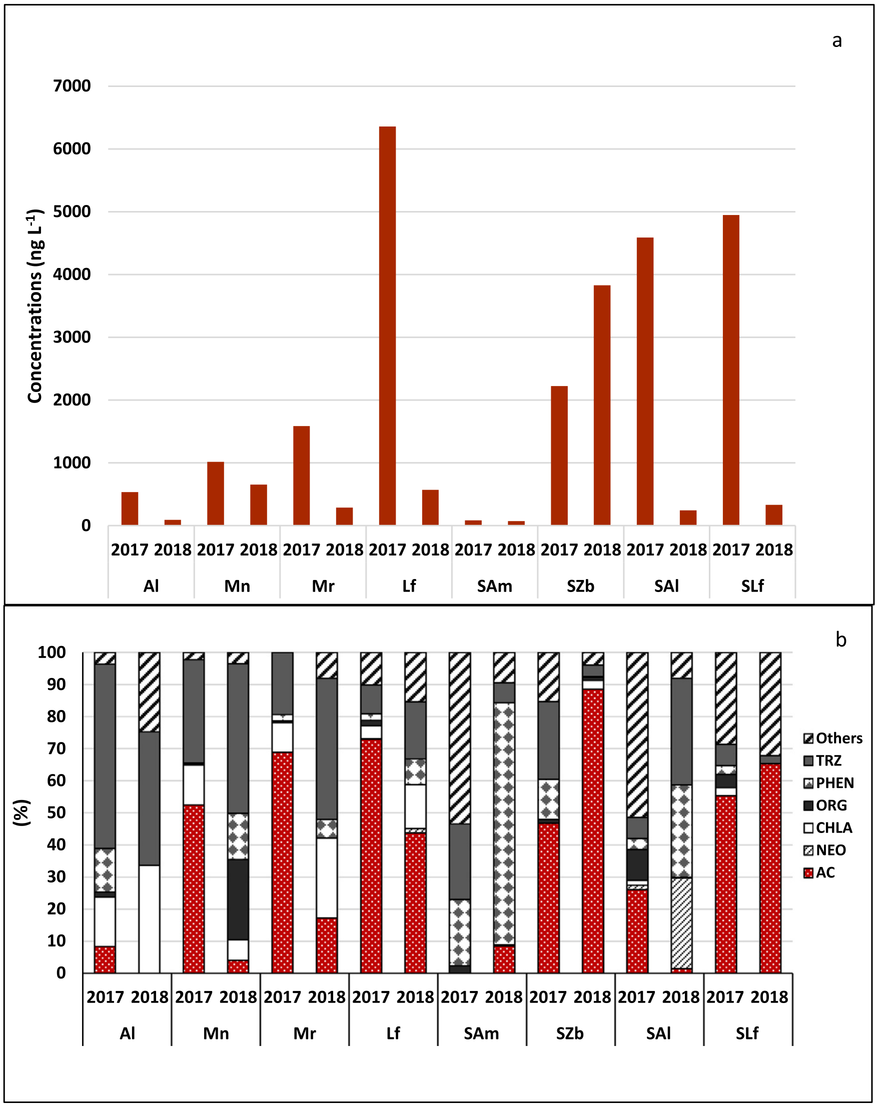

Fig. 4. a) Total concentration of pesticides in the analyzed water samples of the Guadiana Basin (Alqueva reservoir and Guadiana streams); b) Contribution of each class (TRZ: Triazines; PHEN: Phenylureas; ORG: Organophosphates; CHLA: Chloroacetanilides; NEO: Neocotinoids; AC: Acidics) to the total pesticide levels. The class "Others" includes Anilides, Pyridines, Carbamates, Thiocarbamates, Oxidiazoles, Quinolines, Sulfonylureas.

the total acidic pesticides detected in the area). Mecoprop, an acidic herbicide currently not approved for use in Portugal under the EC 1107/2009 (Table S3), was occasionally detected (S_Lf; May 2017: 23 ng L^{-1}). Mecoprop contamination could originate in the Spanish part of the Guadiana Basin, since this active substance was approved for use in Spain until January 2017 and it was detected in the northern part of the reservoir (near the border with Spain). The Acidic herbicides have also been reported to dominate the pesticide contamination profile in water samples from other Mediterranean areas. This is the case of the Ebro River Delta, an area of intensive rice cultivation (Barbieri et al., 2020b). The following most abundant pesticide class was triazines, represented mainly by terbuthylazine (64% of the class) and terbutryn (28% of the class), even though the latter is a substance no longer marketed in the European countries (Table S3). Atrazine, another triazine pesticide banned from the European market, was also occasionally detected in Lucefécit in 2017. Over the years, the acidic class, not detected in 2006/2007, has shown an increasing trend at the reservoir since 2011. In contrast, triazines have declined over time since 2006/2007, when they were the predominant class at the reservoir (Palma et al., 2009, 2014b).

In the temporary streams of Amieira (S_Am) and Álamos (S_Al), the pattern of pesticide contamination in 2017 was different than in 2018. The main contributing class to the total pesticide concentrations in 2017 was “others” in both cases, represented by sulfonylureas and pyridines in S_Am and S_Al, respectively. Phenylurea pesticides dominated the pesticide contamination profile in S_Am in 2018, while triazines, phenylureas, and neonicotinoids were the main classes in S_Al.

Thirty-eight out of the 51 pesticides analyzed were detected/quantified at least once in the basin. The compound with the highest total concentration (i.e., the sum of the concentrations measured in all samples) was bentazone. It globally reached 10,556 ng L^{-1}, occurring mainly at the reservoir in Lucefécit (Lf) (where it reached the maximum concentration of 2509 ng L^{-1}) and in the Lucefécit stream (S_Lf) (Fig. 5). High concentrations of bentazone have also been reported in other Mediterranean basins impacted by intensive agricultural activities (Barbieri et al., 2020b). The following most abundant pesticide was 2,4-D, with a total concentration of 3648 ng L^{-1}, mostly found in the Zebro stream (S_Zb). Despite the high maximum concentrations observed for these compounds, their occurrence was limited to certain areas of the basin (Table S4). Terbuthylazine, with a total concentration of 2202 ng L^{-1}, was the most frequently detected herbicide in the Guadiana Basin (streams and Alqueva reservoir), detected in all locations and also in all sampling campaigns in Mourão (Mr) and Montante (Mn). The high incidence of terbuthylazine could be attributed to its application in corn and sunflower fields, crops that occur all over the year. The ubiquitous presence of terbuthylazine in the reservoir is reported since 2006 (Palma et al., 2009, 2014b). Its concentration was reported to increase in this area from 2006 until 2011/2012, as expected due to the prohibition of atrazine and simazine use in Europe (ECC, 2004a, b). Ten years later, terbuthylazine concentrations are in the same order as those measured in 2006/2007 (39 ng L^{-1} to 85 ng L^{-1}).

Terbutryn also showed a ubiquitous pattern in the Guadiana Basin (Fig. 5). This is of concern because the use of this triazine was banned in Europe in 2002 (EC, 2002). Moreover, it occurred at concentrations above its environmental quality standards (AA (annual average): 65 ng L^{-1}; and MAC (maximum allowable concentration): 34 ng L^{-1} (ECC, 2013)) in the Zebro stream (S_Zb) in 2017.

The presence of banned pesticides in the Guadiana Basin is indeed a worrisome finding, since 23 out of the 38 substances detected are currently not approved for use in Europe (ECC 1107/2009; Table S2), and 5 of them are also priority substances (atrazine, chlorfenvinphos, diuron, simazine, and terbutryn; ECC, 2013). Six of the banned substances

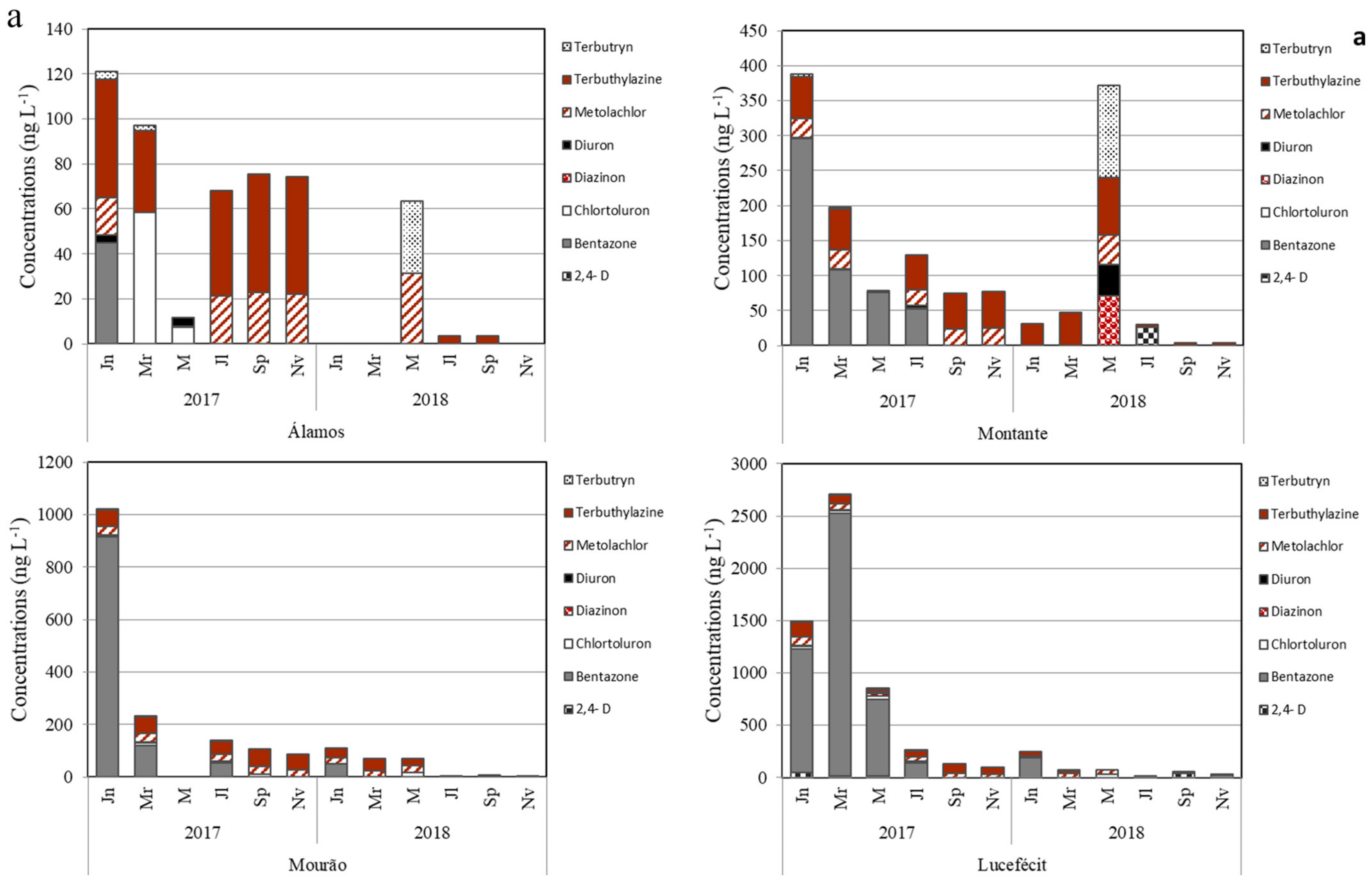

Fig. 5. Spatial (sampling stations) and temporal (2017: drought; and 2018: post-drought) variations observed for the pesticides measured at higher concentrations (ng L^{-1}), and with a detection frequency higher than 30% at least in one location of the Guadiana Basin (a: Alqueva Reservoir; b: Guadiana streams).

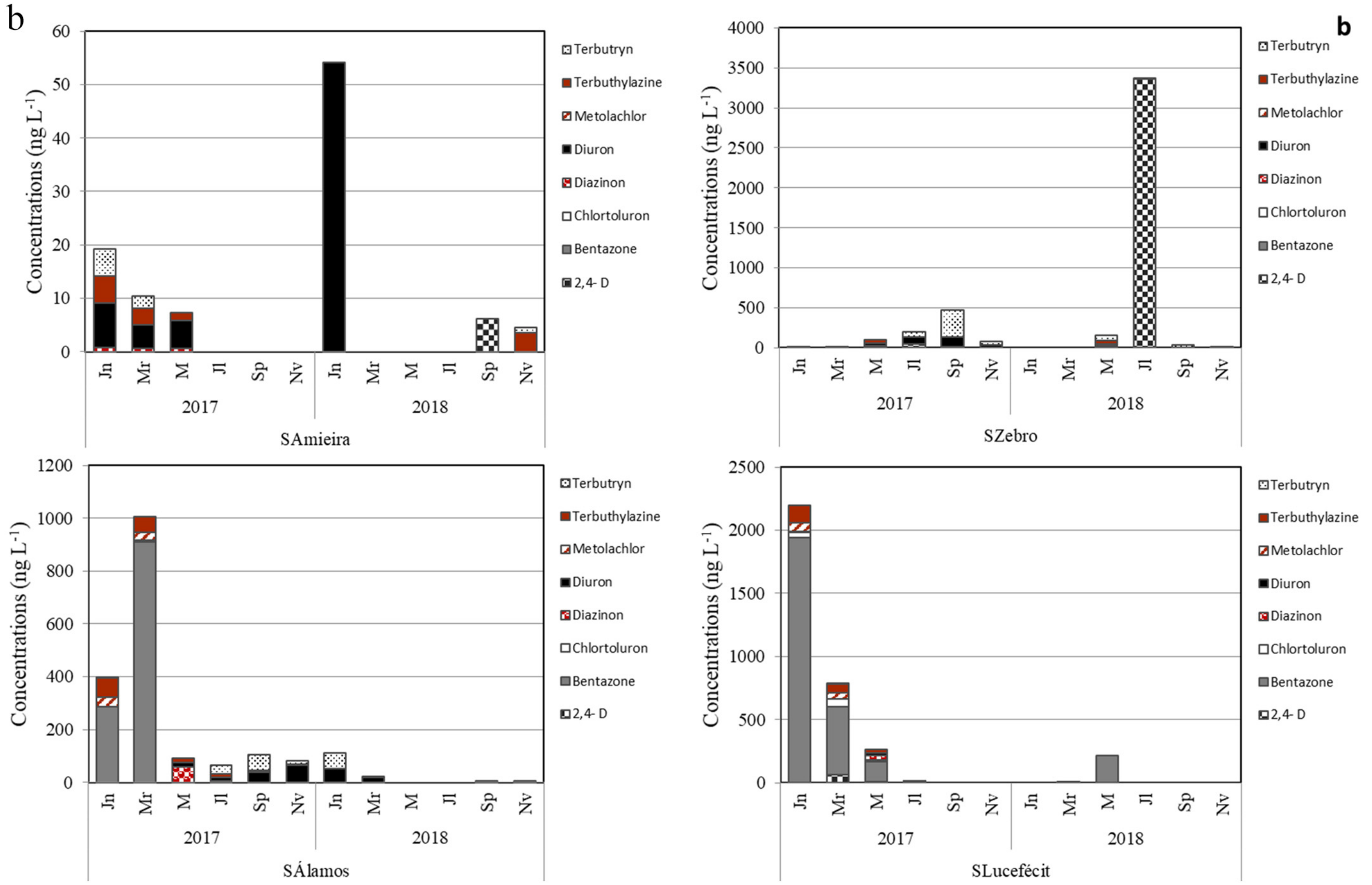

Fig. 5 (*continued*).

detected in the investigated samples, namely, chlorfenvinphos, diazinon, diuron, metolachlor, simazine, and terbutryn, were quantified more than once in several locations in the Guadiana Basin, indicating the existence of a continuous source of contamination. Thus, the presence of these substances could be attributed to their illegal use (metolachlor and terbutryn are not authorized in Portugal since 2003, simazine since 2005, chlorfenvinphos since 2007, and diazinon and diuron since 2009; https://sifito.dgav.pt/) or their release from soils and/or sediments where they could have adsorbed and accumulated during their application in the past due to their physical-chemical properties. The latter may be particularly the case of compounds such as chlorfenvinphos, diazinon, and terbutryn, which are characterized by low water solubility (< 50 mg/L), high octanol-water partition coefficient (log $K_{ow} > 3$), high organic carbon-water partition coefficient (K_{oc} = 500–4000 slightly mobile; $K_{oc} \geq 4000$ non-mobile), and/or long soil half-life times (DT50 > 40 days) (Table S3). Similarly, these compounds are also likely to bioaccumulate in aquatic organisms. This points out the need for assessing the environmental risk that their occurrence may pose to aquatic organisms, and especially, to those species intended for human consumption.

Concerning the pesticides included in the various EU Watch Lists, imidacloprid, when quantified (only in Álamos stream), exceeded the maximum acceptable method LOD of 8.3 ng L^{-1} (EC, 2018), and consequently, its presence may pose undesired effects on aquatic organisms.

3.3. Environmental risk assessment

3.3.1. Environmental risk assessment of target pesticides

Fig. 6 displays the environmental risk of each pesticide in the worst-case scenario (RQex) for each sampling site and period (wet and dry) of each year (2017 and 2018). The corresponding RQex values are provided in Table S5. Thirty out of the 38 pesticides quantified at the basin may pose an environmental risk at least in one of the investigated periods and sites. The pesticide that showed the highest individual risk in the basin was Azinphos ethyl (RQi = 359; S_Lf: May of 2017) followed by 2,4-D (RQi = 168; S_Zb: July of 2018). Bentazone was the pesticide that presented a high risk for aquatic organisms in most sites of the Guadiana basin investigated and in most occasions (17%, 17%, 45%, 17%, and 33% of the samples collected at Mn, Mr, Lf, S_Al, S_Lf, respectively), mainly during the drought year (2017). The referred risk could be attributed to the high concentrations of bentazone found in the water, in line with its common use and moderate degradation (DT50 hydrolysis = 80 days; Table S3). Terbutryn presented a high risk in 42% of S_Zb samples, which may translate into persistent contamination with particularly harmful effects for the aquatic ecosystems of this watercourse. Terbuthylazine presented moderate to high environmental risk in all locations, except in the Amieira stream (S_Am) (with low risk throughout the study period) (Fig. 6). Irgarol showed high risk mainly in the streams in 2017. Chlorfenvinphos and diazinon although detected in relatively low concentrations (< 60 ng L^{-1} in the case of chlorfenvinphos and < 70 ng L^{-1} in the case of diazinon), presented a moderate to high risk (RQex) in streams and in some areas at the reservoir (Montante and Lucefécit), which is of concern, considering that these insecticides have been banned since 2007. The occurrence of dichlorvos, diflufenican, MCPA, metiocarb, and oxadiazon was always associated with a high risk for aquatic ecosystems. In contrast, low and moderate environmental risks were obtained for bromoxynil, chlortoluron, diuron, mecoprop metolachlor, propanil, quinoxyphen, thiacloprode, and methyl tifensulfuron under the worst contamination scenario.

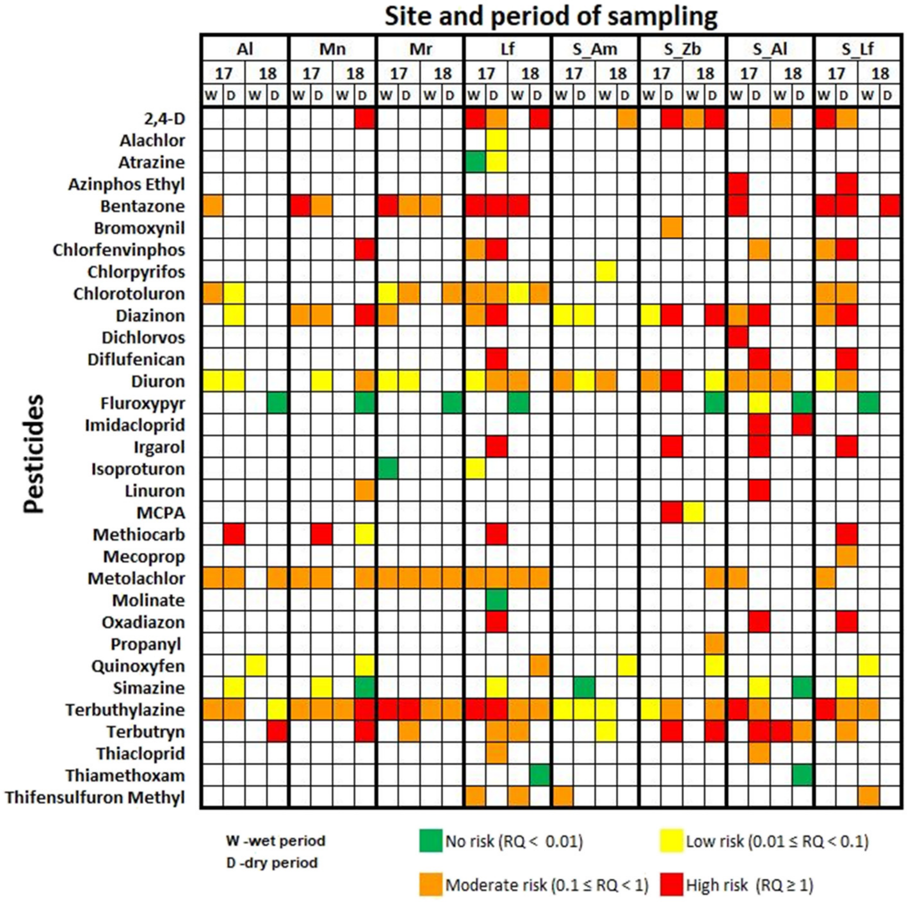

Fig. 6. Risk quotients calculated for each pesticide in the worst-case scenario (RQex), at the eight sampling sites and in the four periods analyzed (Wet and Dry in 2017 and 2018), according to the ranks proposed by Sanchez-Bayo and Baskaran (2002). The raw values are displayed in Table S5.

3.3.2. Guadiana River basin specific pollutants (RBSP)

The pesticides investigated were prioritized to be proposed as the Guadiana RBSPs following the NORMAN methodology. The pesticides having a non-zero ranking score (RS) were ranked and displayed in Table 1, showing the respective contributions of FoE and EoE. Among the 32 pesticides with risk in the basin, 17 showed an RS higher than 0, ranging between 0.26 and 0.01, and hence, proposed as candidates for priority pollutants of the Guadiana Basin. The FoE (number of sites where the concentration surpasses the PNEC) seems to be the dominating factor in the final RS. RS_{EoE} values higher than RS_{FoE}, which indicate high but occasional local ecotoxicological risk effects, were found only in the case of diazinon, imidacloprid, and thiacloprid. Top-ranked pesticides (RS > 0.10) included the herbicides bentazone (#1), terbutryn (#2), terbuthylazine (#4), and the insecticides diazinon (#3), imidacloprid (#5), and thiacloprid (#6). Two of them (terbutryn and diazinon) are no longer on the Portuguese market. Their use is also not authorized in Spain, and thus, transboundary contamination from application can be discarded. However, knowing their sources of contamination is essential to implement the correct mitigation actions. Due to their physical-chemical properties (low solubility <60 mg/L, an octanol-water partition coefficient of 3.7, high organic carbon-water partition coefficient, and relative persistence in soil, especially in the case of terbutryn; Table S3) previously contaminated agricultural soils and sediments can be plausible sources of terbutryn and diazinon contamination in the Alqueva reservoir and associated streams. Terbuthylazine and bentazone are systemic herbicides used in irrigated crops of corn and sunflower. These crops belong to the LULC subclass of annual crops associated with permanent crops (Fig. S1) that have been growing since the construction of the Alqueva reservoir. Regarding neonicotinoids, imidacloprid is used in irrigated vegetables such as tomatoes, and thiacloprid in olive and almond trees, crops very extended in the investigated area. Hence, it is important to work with the farmers and the environmental institutions to improve the environmental sustainability of the use of these pesticides and reduce their potential risk in the Guadiana Basin.

Table 1
Pesticides prioritization based on frequency and extent of exceedance scores (RS_{FoE}; RS_{EoE}), and total score priority ranking (RS).

	RS_{EoE}	RS_{FoE}	RS
Bentazone	0.1	0.16	0.26
Terbutryn	0.1	0.10	0.20
Diazinon	0.1	0.07	0.17
Terbuthylazine	0	0.14	0.14
Imidacloprid	0.1	0.02	0.12
Thiacloprid	0.1	0.00	0.10
2,4-D	0	0.06	0.06
Irgarol	0	0.05	0.05
Methiocarb	0	0.04	0.04
Oxadiazon	0	0.03	0.03
Diflufenican	0	0.03	0.03
Chlorfenvinphos	0	0.03	0.03
Diuron	0	0.02	0.02
Azinphos ethyl	0	0.02	0.02
MCPA	0	0.01	0.01
Linuron	0	0.01	0.01
Dichlorvos	0	0.01	0.01

3.3.3. Spatial and temporal risk in the study area (risk site)

The environmental risk associated with each area of the Guadiana Basin was investigated using an additive model based on the mixtures of pesticides present in each sampling site and year, as reported elsewhere (Barbieri et al., 2020b; Köck-Schulmeyer et al., 2021; Palma et al., 2014a). Fig. 7 presents the environmental risk in each investigated location (RQ*site*: white filled circles) in the risk maps obtained from the spatial analysis, for both years. The Guadiana streams presented a greater risk than the reservoir (except the Amieira stream (S_Am)). These differences in risk were more obvious during the dry period of 2017. This result is relevant, as most streams are temporary and characterized by very sensitive ecosystems associated with high biodiversity. Álamos stream presented the highest quantified risk RQ*site* = 583, in March of 2017, followed by Lucefécit stream with an RQ*site* = 444 in May of 2017. Unlike other sites where the risk was higher in 2017 than in 2018, the Zebro stream presented the highest risk due to pesticide contamination in July 2018. Concerning the reservoir, the highest values of risk were observed in Lucefécit in May 2017. The results showed a temporal pattern, with the greatest risk for aquatic species during the drought year (2017), in line with previous studies in the Guadiana Basin (Palma et al., 2020b). Risk maps allow the spatial

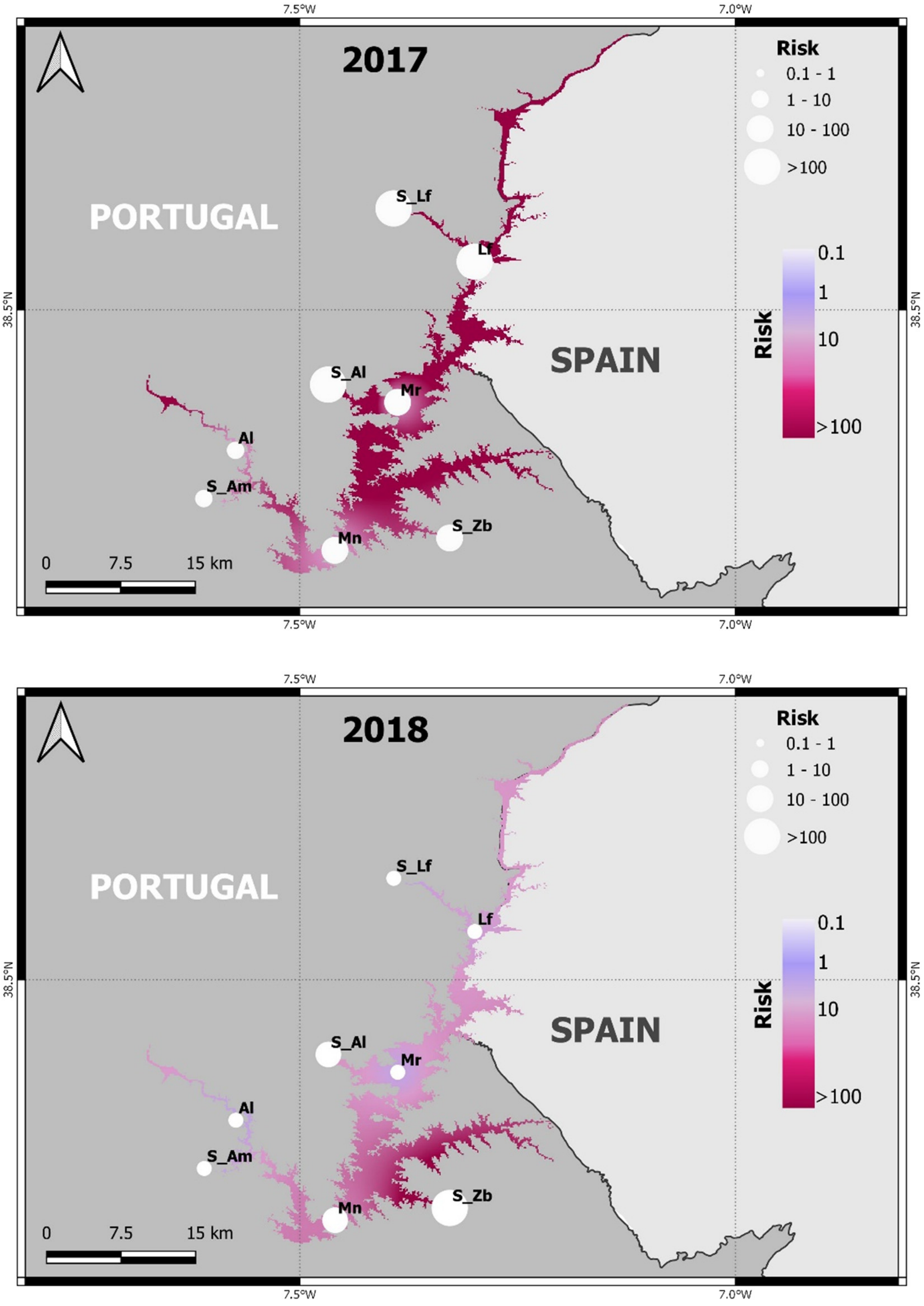

Fig. 7. Risk maps and the respective Risk Quotient (RQsite) calculated via the additive model for the mixture of the 32 pesticides detected within the Guadiana Basin, in 2017 and 2018.

visualization of the environmental risk posed by pesticides in the study area. These maps were obtained through the spatial interpolation of the environmental risk from each site of analysis (RQ*site*). As displayed in Fig. 7, the drought year (2017) presented a higher risk than the post-drought year (2018) in the whole study area. Further, the risk map of 2017 also highlighted the chemical stress of the pesticides in the streams. While the analysis of the risk map obtained for 2017 shows the highest impact on the aquatic ecosystems in the northern part of the study area, the risk map for the year 2018 reveals the highest risk in the southeast of the reservoir.

4. Conclusions

The results of the present study allowed understanding the influence of the land use/land cover and the meteorological conditions on the occurrence and the associated environmental risk of 51 pesticides in the Guadiana Basin. The highest total pesticide concentrations were detected in areas where intensive irrigation agriculture prevails, and olive groves and vineyards are the major crops. The strong drought that occurred during the year 2017 enhanced the impact of pesticides in the aquatic ecosystem of the Guadiana streams, most of them with intermittent regimes, and very sensitive to pollution.

The results showed that 61% of the 38 pesticides quantified in the Guadiana Basin were banned for use in Portugal between 2002 and 2009, and most of them also in Spain, which rules out their transboundary origin. Thus their source could be related to their persistence in sediments and soils during their application in the past. Their presence could also be attributed to the illegal use of the last stock reserves or after purchase of the formulations in other countries (as postulated in the case of mecoprop) countries), or legal application in Spain (as suggested for diuron).

The pesticide environmental risk study showed that 32 out of the 38 pesticides detected were in concentrations that may pose a risk to aquatic species. The greatest environmental risk was observed for azinphos ethyl, banned in Portugal in 2007. Bentazone, terbuthylazine, and 2,4-D were the pesticides whose concentrations could have induced ecological effects in most of the sampled locations and periods. The prioritization exercise allowed concluding that 17 pesticides should be considered in the Guadiana RBSP list, for strict control in the basin. Eight out of the 17 priority pesticides are currently banned for use in Portugal and all of them except diuron are also not allowed in Spain. Thus, understanding their sources is crucial to adopt the appropriate mitigation actions. For instance, in the case of terbutryn and diazinon, which were among the six top-ranked pesticides, their release from agricultural soils and sediments where they may have accumulated after application in the past is the most plausible source. Their potential to accumulate in these matrices is confirmed by their physical-chemical properties.

The environmental risk obtained for each location revealed a greater risk in the streams of the Guadiana Basin than in the reservoir, more evident in 2017 (drought year) than in 2018 (post-drought year). This is of concern due to the high biodiversity associated with this type of hydrological regime and the high sensitivity of these systems to pollution. Agriculture is an economic mover of the Alentejo region, but the results point to the negative effect that this activity may have on the waters of the Guadiana Basin. Consequently, it is crucial to group all the results of pesticides assessment in the region in a platform to support the environmental actions and policies that must be implemented in the basin. Further, the results highlighted the need to work with water management entities to outline actions to reverse the presence of pesticides and with farmers to implement best agricultural practices, to preserve and improve the ecosystem services provided by the Guadiana Basin.

It is important to highlight that due to the transboundary character of the Guadiana basin, pesticide contamination in the study area may be also ruled by extreme events in river runoff, climatological conditions, and pesticide use occurring upstream in the Spanish part. All these factors may have significant effects on the overall water quality in the lower river basin, in terms of sediment loading, total organic content, and chemical composition. The solution to transboundary contamination problems requires adopting transboundary water governance.

CRediT authorship contribution statement

P. Palma: Conceptualization, Investigation, Writing – original draft, Visualization, Writing – review & editing, Supervision, Funding acquisition, Project administration. **S. Fialho:** Investigation. **A. Lima:** Investigation. **A. Catarino:** Investigation. **M.J. Costa:** Writing – original draft, Visualization, Writing – review & editing. **M.V. Barbieri:** Investigation. **L.S. Monllor-Alcaraz:** Investigation. **C. Postigo:** Writing – review & editing. **M. Lopez de Alda:** Supervision, Writing – review & editing.

Declaration of competing interest

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

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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.2021.148703.

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