Science of the Total Environment 774 (2021) 145009

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Pesticide contamination in water and sediment of the aquatic systems of the Natural Park of the Albufera of Valencia (Spain) during the rice cultivation period

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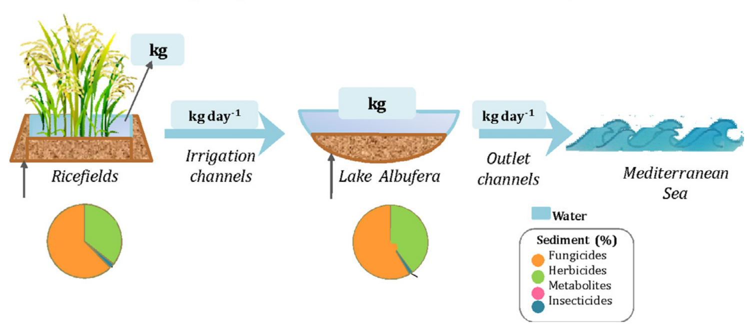
## HIGHLIGHTS

- Same pesticides were detected in water and sediment samples.
- Fungicides and herbicides were ubiquitous during the rice cultivation period.
- Bentazone and tricyclazole were dominant in the four aquatic habitats.
- Pesticide concentrations of higher than 5000 ng L$^{-1}$ were found in water samples.
- Negative effects of pesticides were predicted on the biota of the Albufera Park.

## GRAPHICAL ABSTRACT

Pesticide balance in the aquatic systems of The Natural Park of the Albufera in July 2016.




## ARTICLE INFO

*Article history:*
Received 25 October 2020
Received in revised form 2 January 2021
Accepted 3 January 2021
Available online 2 February 2021

Editor: Damia Barcelo

*Keywords:*
Herbicides
Hydrological cycle
Fungicides
Rice fields
Risk quotient
Mediterranean wetland

## ABSTRACT

The Natural Park of the Albufera (Valencia, Spain) is a Mediterranean wetland where rice cultivation dominates the agricultural activity. The purpose of this study was to offer broader information about the current state of the wetland assessing the contamination by pesticides in four aquatic habitats during the rice cultivation period in 2016. Liquid chromatography with tandem mass spectrometer (UHPLC-MS/MS) was used to determine the pesticides in water and sediment samples from the rice fields, Lake Albufera and irrigation and outlet channels. 21 pesticides were detected in our samples (seven already forbidden by European legislation). Higher values than 10000 ng L$^{-1}$ of accumulated pesticides had been observed in the water samples of the midterm of the cultivation period (July). The sediment samples presented values ten times lower than the water samples. The habitat showed significant differences in the concentrations of the water and sediment samples (Two-way Permanova, $p < 0.05$) at the end and in the midterm of the cultivation period, respectively. Bentazone and tricyclazole were the dominant and most ubiquitous pesticides in the habitats. The quantities also calculated in real water volume showed that the rice fields and Lake Albufera supported more than 100 kg of pesticides in July. Finally, negative effects in the phytoplankton and some taxa of the biota of the Natural Park were predicted in the risk assessment (Risk Quotient >1). The data provided in this work should show concern about the impact of pesticides in Mediterranean systems subjugated to agricultural pressure.



## 1. Introduction

Wetlands are internationally recognized as important aquatic ecosystems due to their biological diversity and are considered to be indispensable to human life. The necessity of their conservation and

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https://doi.org/10.1016/j.scitotenv.2021.145009
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protection is of global concern (Directive 92/43/EEC). The wetlands also have a huge economical value. Agriculture, fishing and tourism are some of their invaluable services. A reduction of 64–70% of their global area has been calculated during the 20th century (Ramsar, 2016). Mediterranean wetlands are the most sensitive ecosystems and are at huge risk of losing their ecological value. The excessive cultivation and massive production have reduced their areas as a result of the agriculture, industrial activity and urbanization in the surrounding areas. The Natural Park of the Albufera of Valencia is an example of a Mediterranean wetland. This aquatic system is one of the most important in the Iberian Peninsula and the Mediterranean zone. It has been protected by Ramsar Convention on Wetlands since 1990, mentioned as a special protection area (SPA) by Birds Directive (Directive 2009/147/EC) since 1991, included in the Natura 2000 network and also classified as Site of Community Importance (SCI) by Habitat Directive (Directive 92/43/CEE) in 2006. The Natural Park of the Albufera has Lake Albufera as one of the most important natural aquatic systems. Lake Albufera's habitat is degraded the most by agriculture, urbanization and industrial activity. Agriculture has had the most negative impact on the lake due to the massive increase of rice cultivation and production in the XVIII century, causing the loss of the 83% of the surface of this lagoon (Romo et al., 2008, 2013; Onandia et al., 2015).

Pesticides are one of the main sources of the accelerated pollution in aquatic ecosystems because of the eutrophication by the excessive nutrient inputs. Thus, the pesticides are classified as pollutants by the Water Framework Directive (WFD, Directive, 2000/60/EEC), considered priority substances by the Directive 2013/39/EU and categorized as dangerous substances by the Directive 2006/11/EC. Pesticide is a broader term that covers herbicides, insecticides, fungicides, growth regulators, repellents, etc. (European Commission, 2020). European normative regulates the pesticides, firstly approving the active substance by the Regulation (EC) N° 1107/2009 and secondly indicating the steps to a sustainable use of the products with the Directive 2009/128/EC (Real Decreto 1311/2012 in Spain). Despite the fact that this legislation was made to avoid bad and excessive use of pesticides, they are being continuously sprayed in huge cultivation areas which sustains an environmental problem in aquatic ecosystems like The Natural Park of the Albufera.

Several studies of pesticides in the aquatic habitats of the Natural Park had been reported previously. The herbicides molinate and thiobencarb had been detected in the water of some irrigation channels, ricefields and Lake Albufera (Carrasco and Planta, 1985; Gómez de Barreda, 1999; Gamón et al., 2002) so as the terbumeton, terbuthylazine and their metabolites together some fungicides (Andreu, 2008; Vázquez-Roig et al., 2010). Organophosphorus insecticides (Boluda et al., 2002) and organochlorine insecticides have also been studied even in the sediment of the lake (Peris et al., 2005). The majority of these chemicals were used commonly in the rice fields but some of them were determined in studies carried out inside the citrus crops area of the wetland (Castillo et al., 2003). The herbicides molinate and thiobencarb, the insecticide fenitrothion or the fungicide flusilazole are some examples of the pesticides studied that are currently not approved under the Regulation (EC) n° 1107/2009. Other studies focused both on the assessment of some of the current pesticides toxicity in the population growth of certain bioindicator species of phytoplankton of the Natural Park (Sabater and Carrasco, 1996, 1997, 1998, 2001; Tarazona, 2001; Tarazona et al., 2003) and on the tolerance level of *Eisenia fetida* to certain pesticides (Rico et al., 2016), *Vibrio fischeri* (Amoros et al., 2000; Boluda et al., 2002), birds and fishes like *Anguilla anguilla* (Carrasco et al., 1972). Microbiological degradation has also been studied by Alonso et al. (1997) with water samples of the wetland. Furthermore, the chemical properties of some fungicides commonly used in the Albufera have been analyzed (Andreu, 2008; Boluda et al., 2013).The mobility, dissipation and accumulation were some of the properties evaluated in laboratory essays and in experimental rice plots (Gamón et al., 2003; Andreu, 2008).

The Natural Park of the Albufera is an agrosystem that works based on the connectivity of the aquatic habitats. The environmental consequences of the pesticide treatment as the contamination of the water and the sediment as well as the toxicological effects in the biodiversity of the ecosystem should be able to be studied as a whole. This last premise was used to study the spatial and seasonal distribution of the contamination by pesticides with the aim to report broader information about the ecological current state of The Natural Park of the Albufera. To fulfill our objective, a wide range of pesticides were determined in water and sediment samples collected in four aquatic ecosystems during the rice cultivation period in 2016. It was also evaluated if the pesticides concentrations obtained could suppose a toxicological risk for some native organisms of the wetland. Finally, the quantity of pesticides in the real water volume and flooded area of the ecosystems studied was estimated. The results of this work may be used as a tool to perform strategies that help to maintain and protect the ecological value of this Mediterranean wetland.

## 2. Methods

### 2.1. Study site

The Natural Park of the Albufera is located on the Mediterranean Spanish coast (39°20′N, 0°21′ W) in the south of the city of Valencia. The Park has an area of 211.2 km$^2$ bordered by the Turia river on the north and Jucar river on the south. It is constituted by several aquatic systems such as Lake Albufera, ricefields, irrigation channels and outlet channels. Lake Albufera is the second coastal lake in the Iberian Peninsula with 23.2 km$^2$ of surface area. It is also shallow (1.2 m of mean depth), oligohaline (1–2% of salinity) and polymictic with an annual renewal rate of 8.4 year$^{-1}$. The Albufera of Valencia is a southern temperate lake with an annual mean air temperature of 18.3 ± 0.1 °C since 1980 and annual mean rainfall of 613.1 ± 88.1mm during a decade until 2016 (Romo et al., 2013). The seasonal rainfall is usually concentrated in the spring and autumn seasons. The water level of the lake is regulated by a wide web of irrigation channels that connect it with the ricefields and by sluice gates situated on its three outlet channels which flow into the Mediterranean Sea (Romo et al., 2005).The Albufera of Valencia works as a water reservoir for ricefields during the flooded periods and as a recipient of the runoff during the drainage periods (Villena and Romo, 2003). The hydrology of the lake and the wetland is bonded to the rice cultivation (Fig. 1) besides the seasonal rainfall

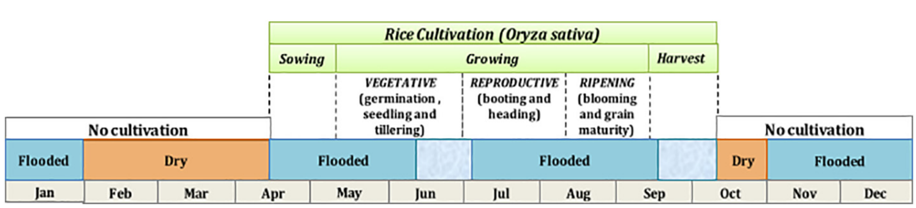



**Fig. 1.** Relationship of the hydrological cycle of the Natural Park of the Albufera and the rice cultivation period during a year. “Flooded” and “dry” indicate the annual hydroperiod of the ricefields and the blue light rectangles point two moments of low water level in the rice fields: the first for the herbicides treatment (June) and the second because of the harvest (September). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Romo et al., 2008, 2013). This relationship between the aquatic systems of the Natural Park is known as connectivity.

The input of the water in the fields usually begins in the middle of April (Resolución n°, 2008/1202) although this moment could be postponed by the Mediterranean climate. For example, at the beginning of May 2016 (the year studied) the ricefields were not completely flooded. The treatment with pesticides follows the biological cycle of the rice (Fig. 1) which could be shorter depending on the varieties of the rice cultivated.

### 2.2. Samples, extraction procedures and analytical method

Water and sediment samples were collected according to the standard methods (APHA, 2011) during the rice cultivation period in 2016. The sampling data was selected according to the representative months of the cultivation period: at the beginning of the cultivation (May), the middle of the pesticide treatment (July) and before harvest (September). The sediment samples only were taken in July. A total of 96 samples, 75 of water and 21 of sediment, were obtained from four aquatic habitats. All samples proceed from 35 sampling points distributed in the ricefields (10), the irrigation channels (11), Lake Albufera (11) and outlets (3) of The Natural Park of Albufera (Fig. 2). The satellite image of the figure and others shown in advance were provided by Earthexplorer website (USGS, 2018). The water samples of the lake were obtained from four representative sampling sites included in the eleven sites of the lake presented in the figure.

The water and sediment samples of this study were transported in a portable freezer to the laboratory where they were stored at −20 °C. The water samples were defrosted for 24 h at room temperature in darkness before the analyses. The sediment samples were transferred into an aluminium box after freezing and freeze-dried during 48 h with Sentry 2.0 lyophilizer from VirTis SP Scientific manufacturer (Gardiner, NY, USA) prior to the extraction.


**Fig. 2.** Location of the sampling sites in 2016. The points number 1 to 11 represent the ricefields and irrigation channels sites except point 4 which was only an irrigation channel. The sampling sites of the ricefields were close enough to the irrigation channels to represent both points in one in the fig. O1, O2 and O3 are the sampling points in the outlets. The sites L1 to L11 belong to the water and sediment samples of Lake Albufera. The satellite image of the figure was captured by Sentinel-2 satellite on 30th of July 2016.

The standards (98–99% purity) of the 68 pesticides analyzed in this study were supplied by Sigma-Aldrich (Steinheim, Germany) (detailed list is provided in Table S1, see Supplementary). The extraction of pesticides for the water samples was carried out using the offline solid-phase extraction (SPE) procedure describe elsewhere (Masiá et al., 2015). The sample volumes of the extraction method were adapted from 50 to 250 mL. The sediment samples (1 g) were extracted by extraction method described previously based on QuEChERS (Carmona et al., 2017).

Pesticides were determined by 1260 Infinity Ultra High-Performance Liquid Chromatography (UHPLC) tandem with a 6410 Triple Quad Mass Spectrophotometer (MS/MS) of Agilent Technologies (Santa Clara, CA, USA). The validation of the analytical method was carried out through recoveries, limits of detection (LOD) and quantification (LOQ), %RSD as linearity and the matrix effect. The pesticides are quantified by the mass spectrometer using Quantitative Mass Hunter Workstation Software (Agilent Technologies, INC.2008). The different MRM transitions used are outlined in Table S3 (Supplementary). Three injections using three different analytical columns and gradients were used. One of them had been previously reported (Ccanccapa et al., 2016; Calatayud-Vernich et al., 2019) and the other two are detailed in Table S4 (Supplementary). Negative ionization was performed to identify the herbicide MCPA. The other two injections were both in positive ionization. One of these injections was performed to identify and analyse a bensulfuron methyl, bentazone, propiconazole and tricyclazole. These pesticides are currently used in rice cultivation in The Natural Park of the Albufera. The other positive ionization served for the determination of the remaining pool. Summarizing, the recoveries for the MCPA and the other four biocides just mentioned ranged from 56% to 120% in water and from 61 to 98% in sediment with a %RSD $< 20$ (Table S5, Supplementary). The development and validation method for the other compounds had been already published (Ccanccapa et al., 2016; Calatayud-Vernich et al., 2019). However, data obtained in the recalibration performed with L'Albufera water and sediment samples are reported in Table S5. The matrix effect showed suppression for bentazone, propiconazole and tricyclazole and enhancement for the bensulfuron methyl and the MCPA in the water (data ranged from −45% to 60%). In case of the sediment, the matrix effect ranged from −58% to 39% with enhancement for the propiconazole and also bensulfuron methyl and the MCPA. The LODs ranged from 0.01 to 5 ng $L^{-1}$ for water and from 0.03 to 1.67 ng $g^{-1}$ d.w. for sediment, and the LOQs from 0.04 to 13.75 ng $L^{-1}$ and from 0.1 to 5 ng $g^{-1}$ d.w., respectively.

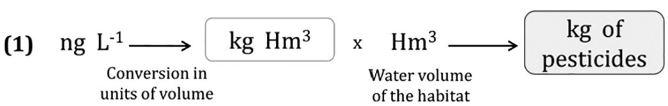
### 2.3. Statistical analyses

Normality of the data was checked prior to statistical analyses with several tests such as Shapiro-Wilk and Anderson-Darling. The concentrations of the pesticides were the variables transformed by decimal logarithm to normalize when it was required. One-way ANOVA test was performed to evaluate whether there were significant differences in the data associated with the data of sampling. Kruskall-Wallis was the non-parametric test performed when the data had no normal distribution despite the standardization. Tukey's or Mann-Whitney post-hoc tests were also used after the previous statistics. Multivariate normality was also tested before the multivariate analyses. MANOVA or Two-way PERMANOVA was used to assess if there were spatial differences between the aquatic habitats and the map location of the sampling points (north and south zone). Two-way PERMANOVA was the non-parametric test selected when normality of the data was not possible. The univariate and multivariate contrast analyses were used on the sum of the pesticide values as biocide types as well as on the concentrations of the pool of compounds to determine the dominant compounds in the water samples and the sediment samples. Classical clustering

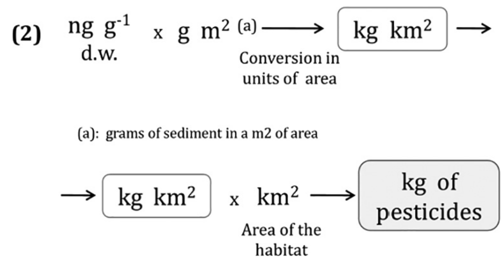
(UPGMA) with Euclidean similarity previously checked the similarity between the samples. Principal Component Analysis with variance-covariance matrix was the other ordination analysis to evaluate the distribution of the water and sediment samples separately, according to the biocide concentrations obtained in every sampling data and during the whole cultivation period. Variance-covariance matrix was selected due to the fact that all the variables were measured in the same units and because the number of samples was higher than the variables so the normality problem could be omitted in case of. The PAST 3.20 (Hammer et al., 2001) was the software used for the statistical analyses.

### *2.4. Hydrological balance of the Natural Park during rice cultivation in 2016*

The quantity of the pesticides accumulated in the water and sediment for the aquatic habitats was calculated in order to estimate the amount of pesticides that The Natural Park of the Albufera supported during the rice cultivation period in 2016.The hydrological balance was calculated in the water volume of every ecosystem separately using the concentrations in ng $L^{-1}$ in the water samples (Diagram 1) and were obtained in flooded area of the rice fields through imagery analytical methods (Soria et al., 2015) with Landsat 8 or Sentinel-2 satellite images from the Earthexplorer website (USGS, 2018).




The amount of pesticides by area in the rice fields (flooded area) and the Lake Albufera were solved with the initial data in ng $g^{-1}$ in dry weight (d.w.) of the sediment samples. The mass of sediment by $m^2$ was calculated considering that the thickness of sediment is 2.5 cm. The values in g $m^2$ were the conversion data used to obtain the amount of pesticides (kg) by flooded area ($km^2$) (Diagram 2).




The water flows ($hm^3$ $day^{-1}$) served to obtain the pesticide concentration (kg $day^{-1}$) in the irrigation and the outlet channels. The hydromorphological data of the channels was measured in situ to calculate the water flows.

### *2.5. Risk assessment*

Risk Quotient (RQ) was used to assess the environmental risk in the water samples of the aquatic ecosystems of The Natural Park of the Albufera according to the European technical guidance document on risk assessment (EC, 2003). Acute ($EC_{50}$) and chronic concentrations (NOEC) needed for the calculations were obtained from OPP Pesticide Ecotoxicity Database (2020). This database was chosen due to the wide range of organisms on which pesticide toxicity has been tested. Finally, the indexes were calculated for the three target organisms commonly tested algae, *Daphnia magna* and fish. In addition, several organisms representative of The Natural Park of the Albufera

**Table 1**
Mean, standard error (std. error), maximum (max), minimum (min) and number of samples (n) of the pesticides detected in water and sediment samples of The Natural Park of the Albufera during rice cultivation period in 2016. The pesticide concentration in the sediment samples were calculated in dry weight (d.w.).

| Pesticides | All habitats: Water (ng $L^{-1}$) Mean | Std. Error | Max | Min | n | Sediment (ng $g^{-1}$ d.w.) Mean | Std. Error | Max | Min | n |
|---|---|---|---|---|---|---|---|---|---|---|
| **Herbicides** | | | | | | | | | | |
| Bensulfuron methyl | 30,2 | 3,2 | 114 | 2,9 | 56 | 24,9 | 1,0 | 26,8 | 23,5 | 3 |
| Bentazone | 4119 | 616 | 12668 | 26,2 | 43 | 82 | 43 | 898 | 11,5 | 20 |
| Diuron | 9,8 | 1,9 | 19,1 | 4 | 7 | 1,0 | 0 | 1,0 | 1,0 | 1 |
| MCPA | 144 | 13,1 | 495 | 15 | 74 | | | | | |
| Propanil | 14,5 | 2,7 | 50,7 | 0,8 | 27 | 1,2 | 0,3 | 2,1 | 0,1 | 7 |
| Terbumeton | 0,9 | 0,2 | 3,2 | 0,2 | 13 | | | | | |
| Terbutryn | 4,2 | 0,8 | 8,1 | 2,7 | 6 | | | | | |
| **Herbicide metabolites** | | | | | | | | | | |
| Terbumeton deethyl | 11,3 | 1,4 | 63,9 | 3,1 | 50 | 0,4 | 0 | 0,4 | 0,4 | 1 |
| Terbuthylazine 2-hydroxy | 7,9 | 0,6 | 23,2 | 1,5 | 54 | 0,4 | 0,1 | 1,3 | 0,1 | 10 |
| Terbuthylazine deethyl | 8,2 | 2,0 | 23,1 | 2,0 | 12 | | | | | |
| **Insecticides** | | | | | | | | | | |
| Acetamiprid | 26,1 | 5,4 | 185 | 1,4 | 45 | 2,3 | 0,7 | 8,7 | 0,4 | 12 |
| Diazinon | 3,6 | 0,8 | 10,9 | 0,6 | 13 | 0,2 | 0,02 | 0,2 | 0,1 | 4 |
| Ethion | 3,3 | 0,5 | 9,7 | 0,6 | 19 | 1,0 | 0,2 | 2,8 | 0,1 | 21 |
| Imidacloprid | 20,6 | 2,5 | 78,2 | 3,2 | 38 | 7,4 | 4,5 | 25,2 | 1,7 | 5 |
| **Fungicides** | | | | | | | | | | |
| Carbendazim | 20,8 | 5,7 | 81,8 | 2,9 | 19 | 1,9 | 0 | 1,9 | 1,9 | 1 |
| Imazalil | 29,1 | 8,3 | 164 | 2,3 | 21 | 3,3 | 0,6 | 8,5 | 0,9 | 16 |
| Prochloraz | 410 | 124 | 3435 | 2,1 | 47 | 27,4 | 8,9 | 123 | 0,3 | 21 |
| Propiconazole | 296 | 63,4 | 2712 | 23,2 | 54 | 20 | 3,0 | 62,3 | 2,2 | 19 |
| Tebuconazole | 183 | 20,5 | 754 | 9,7 | 66 | 9,0 | 2,3 | 41,1 | 0,5 | 20 |
| Thiabendazole | 15,4 | 2,1 | 56,7 | 0,8 | 57 | 2,0 | 0,3 | 7,1 | 0,4 | 20 |
| Tricyclazole | 1704 | 342 | 21623 | 10,6 | 70 | 81 | 34,8 | 739 | 0,9 | 21 |

(Table S6, Supplementary) were considered in order to obtain wider information of the risk assessment. The table details the taxonomic groups of the organisms studied, the species from the OPP database in which $EC_{50}$ and NOEC values were used and the references where the organisms of the Natural Park were previously reported (Antón-Garrido et al., 2013; Blanco et al., 2003; Burillo, 1999; Olmo, 2016; Romo et al., 2005; Romo and van Tongeren, 1995; Rueda et al., 2005, 2006; Blanco and Romo, 2006).

## 3. Results

### 3.1. Pesticides detected in the samples of the Natural Park of the Albufera

The HPLC-MS/MS analyses detected a total of 21 pesticides of the 68 studied (31%) in the water and sediment samples of the Natural Park of Albufera collected during the rice cultivation period in 2016. The compounds identified were 7 herbicides, 3 metabolites of herbicides, 4 insecticides and 7 fungicides (Tables 1 and S2, Supplementary). The 21 pesticides were detected in the water whereas 17 pesticides were found in the sediment of The Natural Park of the Albufera (Table 1). The water samples of the ricefields and the irrigation channels had the widest range of the pesticides identified above the samples of the Lake Albufera and the outlets (see Supplementary, Table S7). The sediment samples of the ricefields also had the maximum number of pesticides in contrast to the lake.

The 73% of the pesticides detected remained during the cultivation period in the water of the four aquatic habitats (Fig. 3B). The biggest pesticide determination was of 89% in the water samples of July and 100% of the 21 pesticides detected were found in the ricefields and the irrigation channels (Fig. 3A). The fungicides were the most frequent compounds in the habitats with 80–100% of the water and sediment samples containing them during the cultivation period (Fig. 3B and C). The herbicides were less frequent in water (56%) and sediment samples (29%). The three metabolites determined in this study could belong to the herbicides terbumeton and terbuthylazine but only the terbumeton was found in the water samples. The metabolites were analyzed in the samples of the whole cultivation period although their concentrations were lower than the other pesticides with a mean of $9.4 \pm 0.7$ ng $L^{-1}$ in the water samples and $0.4 \pm 0.1$ ng $g^{-1}$ in the sediment samples (Table 1). Finally, the four insecticides had an average of 50% occurrence in both types of samples (Fig. 3B and C).

### 3.2. Water samples and rice cultivation period

The results of water samples analyzed revealed that The Natural Park of the Albufera accumulated pesticides in concentrations higher

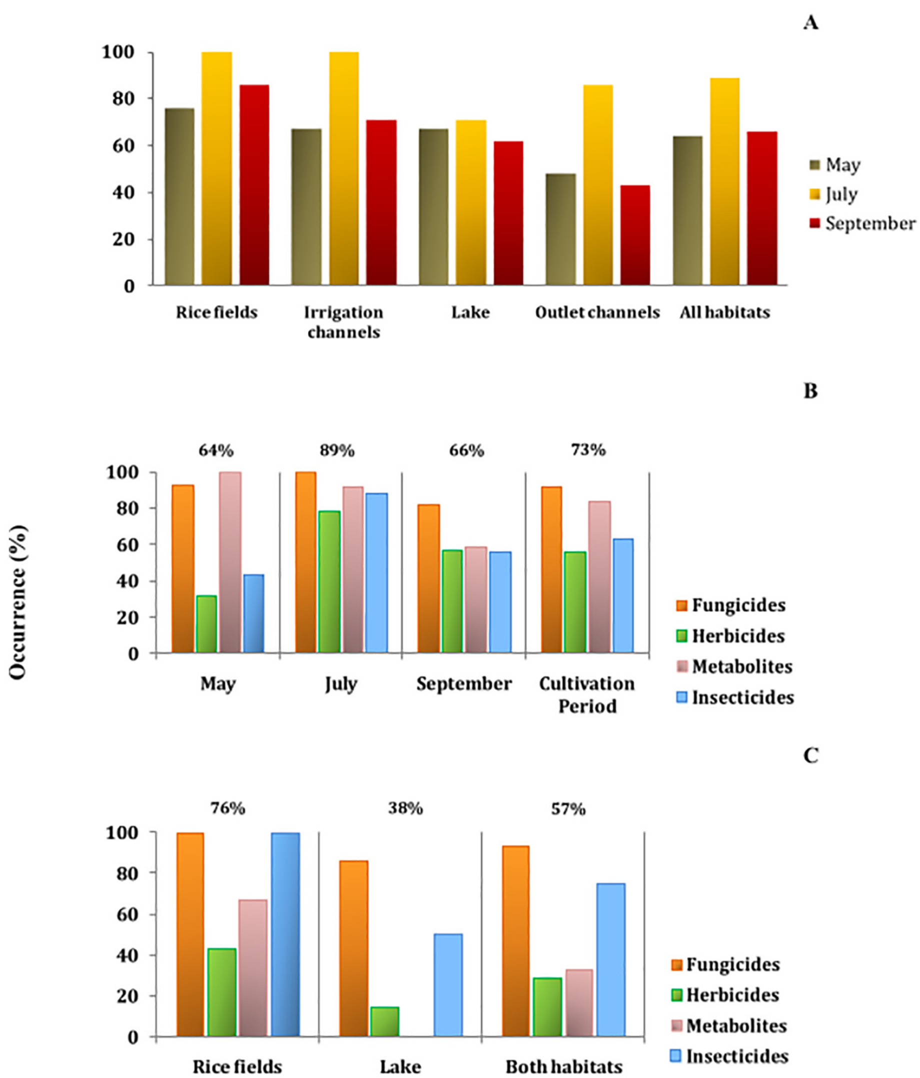



**Fig. 3.** Pesticide occurrences (%) in the water samples collected during the rice cultivation in 2016. A) Occurrence from the total number of the pesticides detected in the water samples of the four aquatic habitats in May, July, September. B) Percentage occurrences of the four pesticides groups in the water samples and C) in the sediment samples. The percentages above the bars in B and C are the global occurrence of the pesticides in every month (B) and in the habitats (C) where sediment samples were collected.

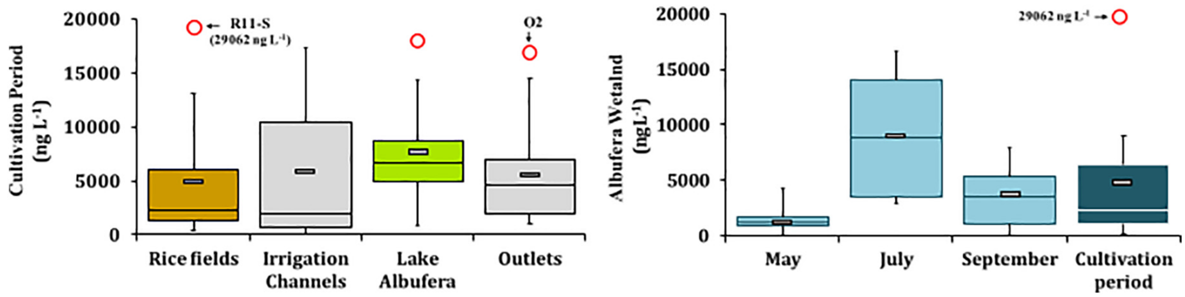



**Fig. 4.** Spatial and seasonal distribution (left and right figures, respectively) of pesticides concentrations in the water (ng L$^{-1}$) in the aquatic habitats of The Natural Park of the Albufera during rice cultivation period in 2016. The boxes on the left show the accumulated concentrations obtained in the whole cultivation period in every aquatic habitat. The boxes on the right represent the accumulated concentrations of the four habitats together in the three sampling months and the complete period. The value of the outliers (red circles) are indicated when they surpass the scale of the vertical axis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

than 10000 ng L$^{-1}$ with mean concentrations in the four aquatic habitats studied around the range of 5000 to 7800 ng L$^{-1}$(Fig. 4). The highest concentrations belong to the midterm of the cultivation period in July.

The outlier value of 29062 ng L$^{-1}$ was a positive analytical measure (Figs. 4 and 6) determined in a water sample of a ricefield at sampling point 11.72% of the accumulated fungicides concentration belonged to the tricyclazole (Tables 1 and S7). The maximum concentrations of fungicides were below 4000 ng L$^{-1}$but despite making an overestimation in the results the data was included in the statistical analyses. At the beginning of the cultivation period the water samples accumulated between 1000 and 5000 ng L$^{-1}$ in most of the sampling points (Fig. 5). The maximum values calculated in this study were found in the 64% of the sampling points in July. The north points 1 and 2 had accumulated concentrations of around 10000 ng L$^{-1}$ even in September. The samples of the south zone (points 8 to 11) maintained the range 1000–5000 ng L$^{-1}$. The progressive accumulation in the pesticides concentrations over the cultivation period is also observed (Fig. 5).

First multivariate and contrast analyses were performed on the matrix data where pesticide concentrations were organized by accumulated values in the three sampling data (May, July and September). PCA scatter distributed the water samples in two main groups (Fig. 7). The first group joined the samples with the higher concentrations in the sampling points 1, 2, 8–11 and Lake Albufera and the outlet Perellonet (O2). The second group had points 3 to 7 with the other outlets. The PCA explained the 89% of the variability of the data with the first component. The component 1 defined as July was significantly different from May and September (Tukey's post-hoc = 8.86, $p < 0.001$). These results could be related to the many treatments used in the midterm of the cultivation period. The sample R11-S was distant from the other samples because of the outlier value of the tricyclazole. The contrast analyses did not point significant differences in habitat or north and south zones in accumulated concentrations of the whole period (Two-way PERMANOVA, $F = 0.05$ and 0.06, respectively, $p > 0.05$). The cluster analysis ordered the samples as with the PCA in a tree diagram with a correlation of 0.83.

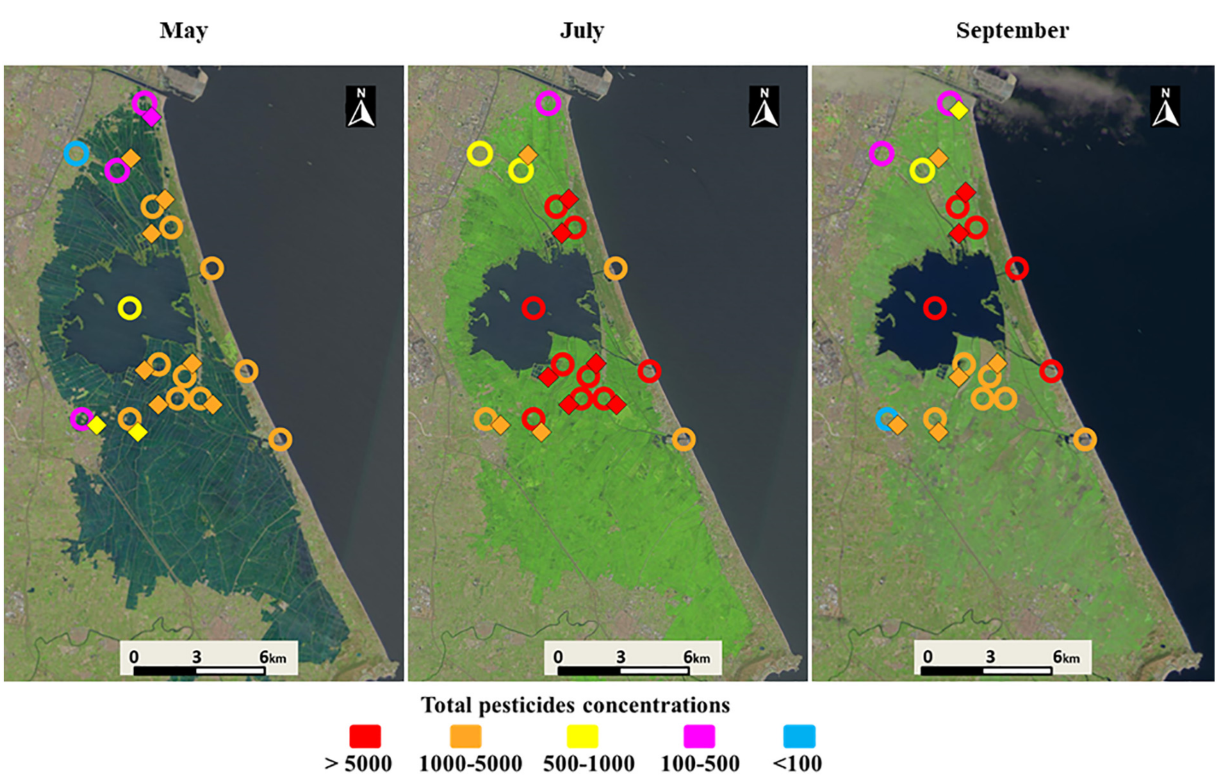



**Fig. 5.** Accumulated concentrations (ng L$^{-1}$) of the pesticides determined in water samples during rice cultivation in 2016. The circles represent the concentration of pesticides in the channels and Lake Albufera. The diamonds indicate the accumulated values in the ricefields. The diamonds indicate the accumulated values in the ricefields. From left to right, the satellite images were obtained from the Sentinel-2 on 21st May, 30th July and 18th September 2016.

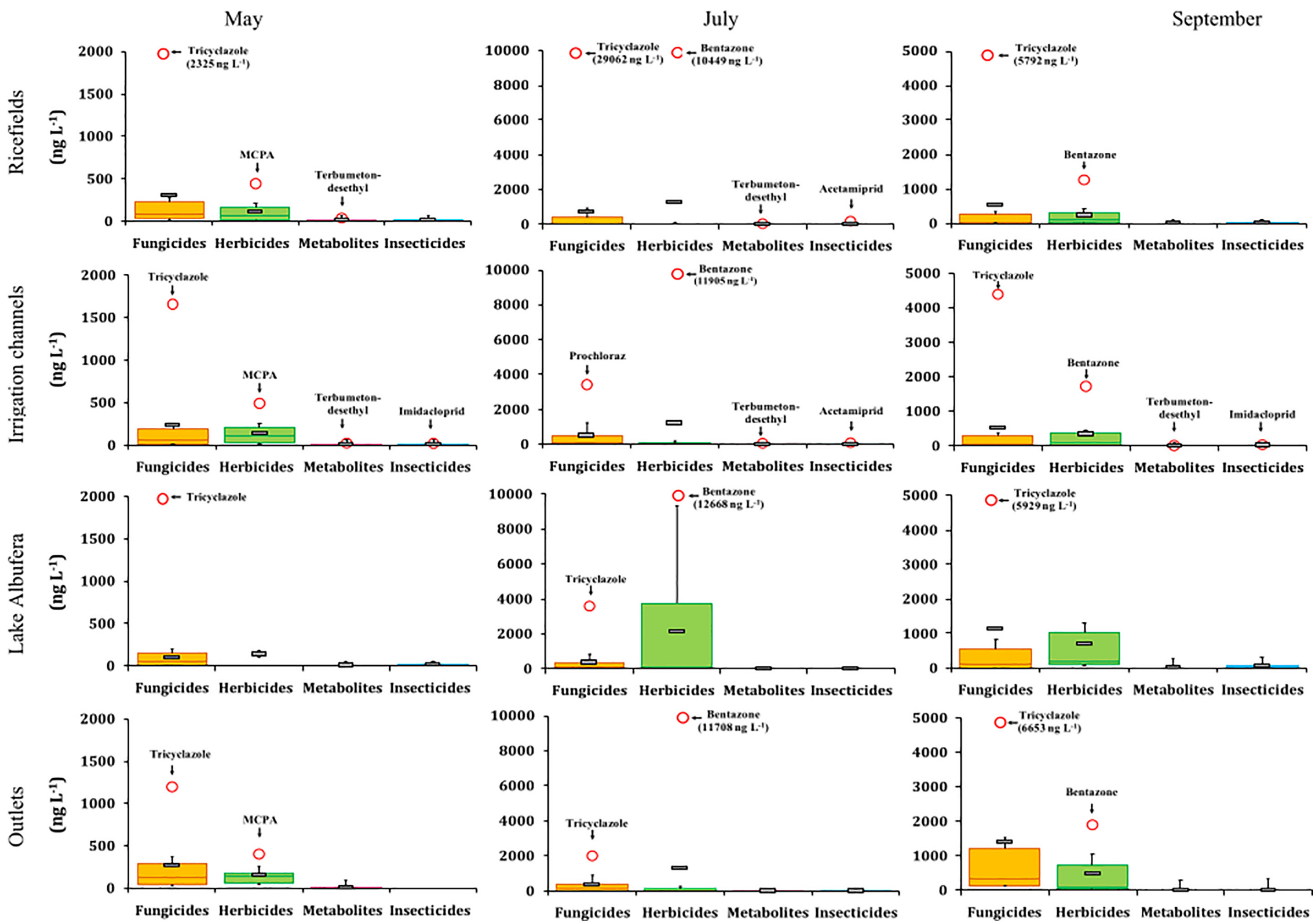



**Fig. 6.** Pesticides concentrations in water samples (ng $L^{-1}$) in the four habitats of The Natural Park of the Albufera in the three sampling data during the rice cultivation period in 2016.

The contrast analyses pointed to the fungicides and the herbicides as the abundant groups in the water samples (Tukey's post-hoc: $p < 0.001$ in July; Mann-Whitney post-hoc: $p < 0.001$) remarking the fungicides in May and September (Mann-Whitney test: $U = 111$, $p < 0.001$). The lake Albufera and the outlets had higher concentrations in September mainly due to the tricyclazole in the outlets (Fig. 6). This could be expected in the harvest period when both systems receive the water drained from the ricefields. The main compounds that remained in these habitats were the fungicides with concentrations approximately five times higher than herbicides (Table S7). Three PCA scatter plots by sampling data were performed with a matrix of the total concentrations of the four pesticides groups. All of them explained more than the 90% of the variability of the data with the first component (Fig. 8). The first component was represented by the fungicides and the second by the herbicides in the three analyses. The water samples of the ricefields and the irrigation channels from points 1–2 and 8–11 had the highest concentrations. Their relationship with the herbicides and fungicides vector changed depending on the sampling data. This group also had peak concentrations in Lake Albufera as in May as in July. The outlets also had extreme values in July due to the fungicides and herbicides. The concentrations of the second group highlighted in the Perellonet outlet (sample O2) (Fig. 6). The Cluster analysis grouped the samples based on their similarity of the pesticides concentrations in a progressive order of concentration.

The correlation values were 0.78 in May, 0.93 in July and 0.74 in September (cluster not presented). The multivariate contrast test Two-way PERMANOVA used on the three matrixes did not point significant differences to conclude that the type of habitat or the north and south zones had any influence with the variability of the pesticide concentrations in the water samples. The matrix data analyzed separately in each month neither show differences by some of the two factors in May ($F = 0.01$ (zone) and $F = 0.07$ (habitat), $p > 0.05$). Our results from the matrix data of July did indicate significant differences in the fungicides and the herbicide metabolites concentrations by zone ($F = 3.3$, $p < 0.1$ and $F = 6.7$, $p < 0.05$, respectively). The most significant differences were detected in the data of September by both factors ($F = 0.37$ and $p < 0.05$ for zone, and $F = 0.41$, $p < 0.05$ for habitat). The post hoc analyses also showed the outlets as the aquatic ecosystems with the significant differences (Pairwaise, $p < 0.05$).

Six pesticides were found as the most common and abundant in the water samples during rice cultivation. They were the herbicides bentazone and MCPA and the fungicides tricyclazole, tebuconazole, prochloraz and propiconazole. These compounds presented significant differences by habitat (Two-way PERMANOVA: $F = 3.55$, $p < 0.05$) and by sampling data (Two-way PERMANOVA: $F = 27.75$, $p < 0.001$).

The bentazone and the tricyclazole were the dominant compounds in the water samples in the cultivation period (Mann Whitney post-hoc: $p < 0.001$). The bentazone was also the dominant pesticide in July and the tricyclazole dominated in May and September. The MCPA was the most frequent herbicide in May ($215.2 \pm 23.5$ ng $L^{-1}$) whereas the bentazone was absent. However, the bentazone was the dominant of the herbicides in the cultivation period remaining. The MCPA concentrations dropped a mean of four times in the habitats two months later ($58.2 \pm 7.5$ ng $L^{-1}$) but kept 99% of occurrence in the water samples. The values of this herbicide were similar to May at the end of the period and the maximum concentrations (350–400 ng $L^{-1}$) were found in the samples of ricefields and the irrigation channels in the north.

The fungicide tricyclazole was dominant from the beginning of the cultivation in the four aquatic systems in 88–100%. The peak values were observed in September and ranged from 3300 to 6600 ng $L^{-1}$ in the channels and rice fields and 5900 ng $L^{-1}$ in the Lake Albufera.

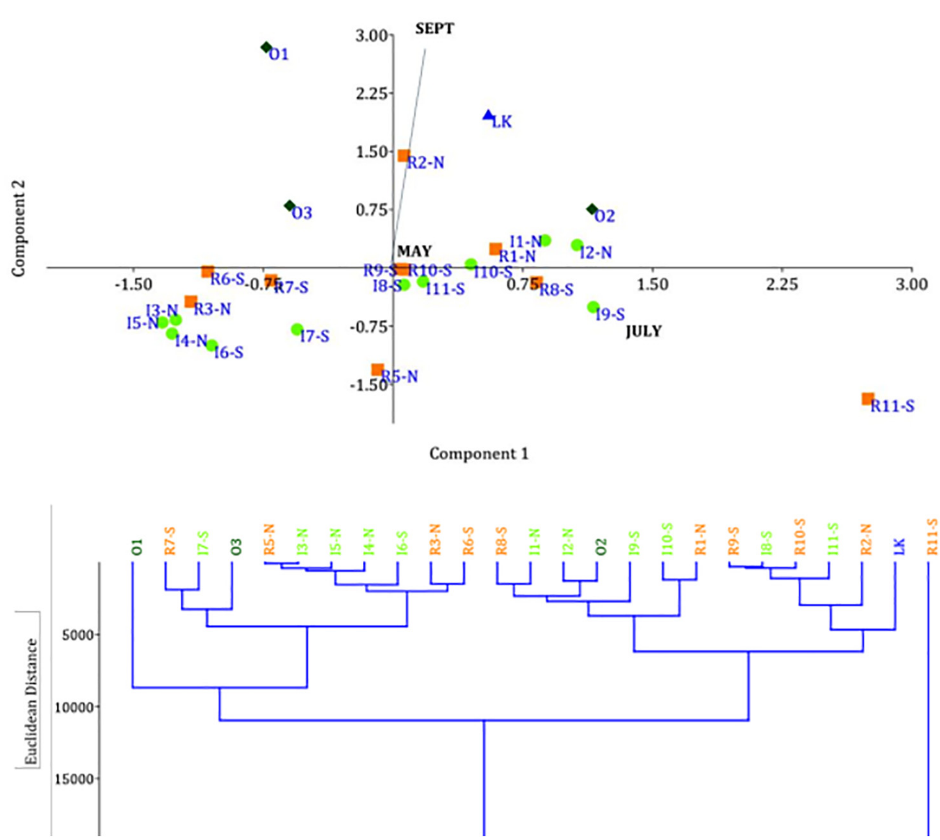



**Fig. 7.** PCA scatter plot and Cluster diagram of the water samples with accumulated concentrations of pesticides in the cultivation period. The vectors May, July and Sept (September) represent the sampling data. Legend: R for ricefields (orange squares), I for irrigation channels (green dots), O for the outlets (dark green diamonds) and LK for the lake (blue triangle). N and S at the end of the label are North and South sampling zones. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

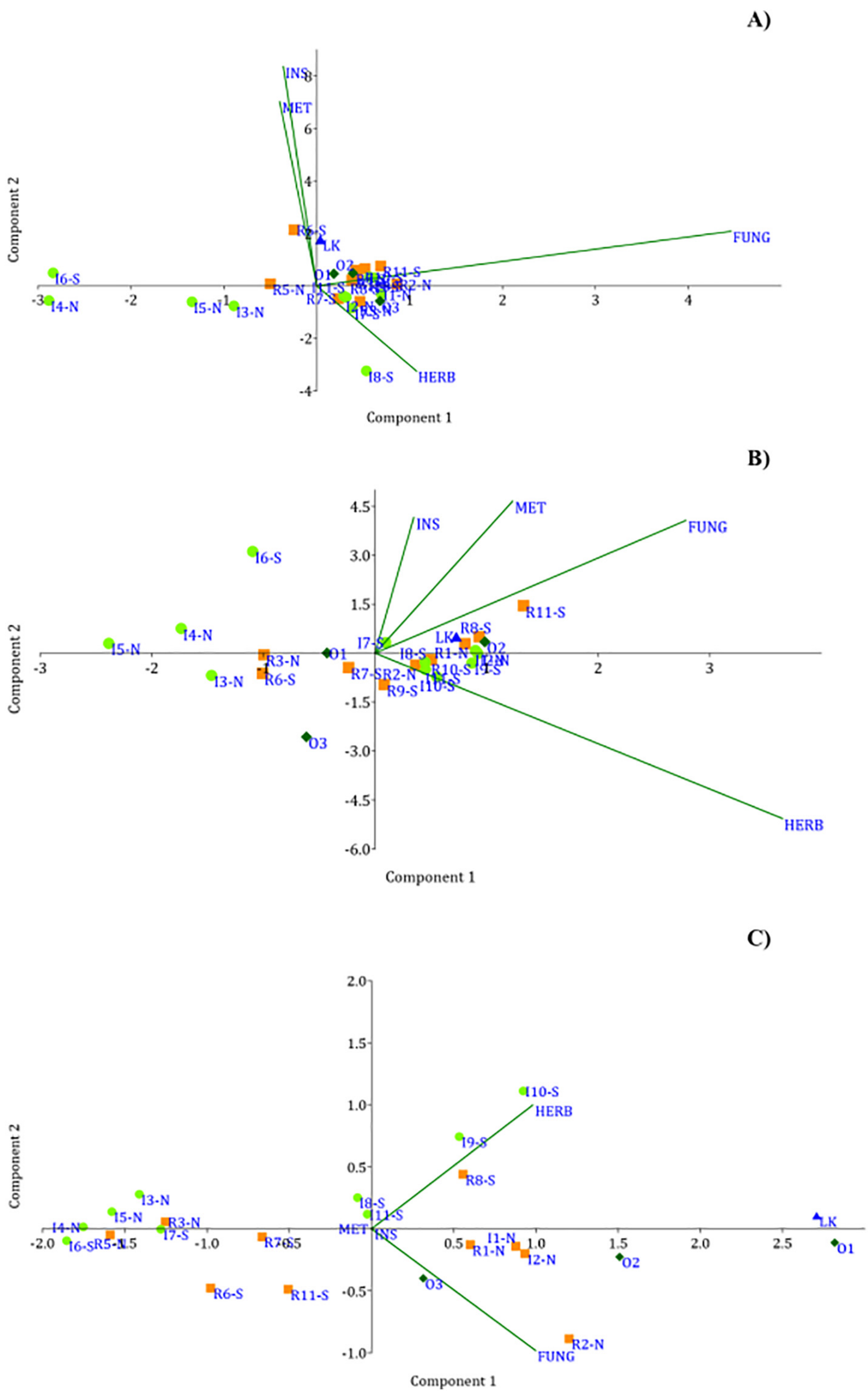



**Fig. 8.** PCA scatter plots of the water samples distributed by the accumulated concentrations of the four pesticide groups in the three sampling data (A, May; B, July; C, September). Vectors legend: herbicides (HERB), metabolites (MET), insecticides (INS) and fungicides (FUNG).

### 3.3. Sediment samples

The sediment samples were collected in ricefields and Lake Albufera in the midterm of the cultivation period in 21 sampling points (Fig. 9). The sediment samples of the ricefields were collected at the same points as the water samples. The HPLC-MS/MS analyses determined a total of 17 pesticides in the sediment samples and that they were the same compounds as those analyzed in the water samples. The rice fields and Lake Albufera had 76% and 38% of the total number of pesticides identified in this study, which means a difference of 24% and 33% from the pesticides found in the water samples (Fig. 3B and C). The pesticide concentrations in the sediment samples were mostly below 500 ng $g^{-1}$d.w. with the exception of two sediment samples of two rice fields at the north of the Natural Park (Fig. 9). The samples of the lake closest to the exit of the irrigation channels also presented concentrations between 100 and 500 ng $g^{-1}$d.w. These punctual differences were not enough to showed significant differences between the north and south zone in the samples (Two-way PERMANOVA: $F = 1.24$,


**Fig. 9.** Accumulated concentrations of pesticides in the sediment samples of the ricefields (diamonds) and Lake Albufera (circles) in July 2016. The concentrations were obtained in dry weight of sediment (ng $g^{-1}$d.w.).

$p > 0.05$). The concentrations of pesticides accumulated in the rice fields (35 ± 0.7 ng $g^{-1}$ d.w.) quadruplicate the concentrations of the Lake (9.5 ± 1.3 ng $g^{-1}$d.w.).

The Cluster analysis grouped the sediment samples in three main clusters with 0.98 of correlation. One of the groups had almost all of the lake samples. The difference between the other two samples of the Lake and the samples of the ricefields was the concentration in fungicides. Only 50% of the pesticides determined in the sediment samples were detected in Lake Albufera (Two-way PERMANOVA: F = 6.56; $p < 0.001$).

The common and ubiquitous pesticides in the sediment of these systems were the bentazone and the four fungicides prochloraz, propiconazole, tebuconazole and tricyclazole. The dominant compounds were the bentazone and the tricyclazole (Fig. 10) just as in the water samples. The bentazone turned out to be the only herbicide with 100% of occurrence and the most significantly different over the fungicides (Mann-Withney post hoc: $p < 0.05$). No herbicide metabolites were detected. The PCA analysis of the sediment samples explained the 99% of the variability of the data with the two first components. The first component (60%) separates the ricefields from Lake Albufera due to the concentrations of fungicides. The second axis (39%) defined the variability of the data between the herbicide values (Fig. 11). There were significant differences between the pesticide groups (One-way ANOVA: F = 52.9, $p < 0.001$) The R1-N had up to nine times more accumulated concentration (> 900 ng $g^{-1}$d.w.) than the remained samples.

The bentazone in this sample was higher than 800 ng $g^{-1}$ d.w. The insecticides were found in lower concentrations than the herbicides and fungicides (Tukey's test post hoc: $p < 0.001$). The Spearman correlation analyses were performed on the majority of common pesticides in the pool of sediment samples. Three stronger positive correlations (0.7–0.89) associated the pairs imazalil-tebuconazole and prochloraz-tebuconazole. The last one joined the bentazone with the prochloraz and the tricyclazole.

### *3.4. Hydrological balance of the Natural Park during rice cultivation in 2016*

Hydrological measures of the four aquatic ecosystems studied were used to estimate the real magnitude of the quantity of pesticides in their water volume, water flow and flooded area that The Natural Park of the Albufera supported during the rice cultivation in 2016. Previously, pesticide concentrations were calculated in the proper units for water volume ($hm^3$) and for area (ha) from the total concentrations obtained by habitat and sampling month. Real water volume and flooded area of rice fields and Lake Albufera were measured by imagery analytical methods and the water volume and water flow for the channels and outlets measured in situ in the field. The figure below represents the quantities of pesticides estimated in the water and the sediment of the aquatic habitats studied in the Natural Park of the Albufera in the midterm of the rice cultivation period (Fig. 12).

The initial values of pesticides in both habitats in July were around 9 kg $hm^3$ and also in the irrigation and outlet channels. At that time, approximately 12800 ha of rice fields were flooded with 15.3 $hm^3$ of water while Lake Albufera had almost 21 $hm^3$ of water volume. Lake Albufera had 30% more pesticides than the rice fields (142 kg). This means that the relationship of the kg of pesticides between these two habitats is explained by the difference in their water volumes at this moment of the cultivation period. The maximum amount of pesticides in the Lake was reached in September with 227 kg whereas at the beginning of the cultivation there was 5.3 kg. The outlets are not usually opened in July so in the figure an estimation of the monthly output to the Mediterranean Sea is indicated.

The 50–60% of the pesticide amount in the water of the wetland was due to the herbicides but Lake Albufera had near 80%. The opposite was observed in the sediment of the lake as well as in the rice fields where the fungicides were the most accumulated. The percentages of

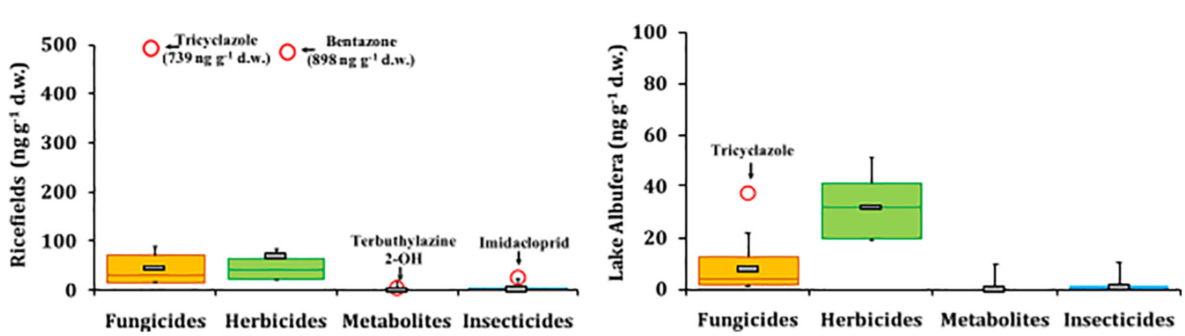



**Fig. 10.** Concentrations of the pesticides groups in the sediment samples of the ricefields and Lake Albufera in July 2016. The concentrations were obtained in dry weight of sediment (ng $g^{-1}$d.w.). Red circles indicate the outliers. The values of the outliers are only pointed when the outlier appear out of the concentration scale. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

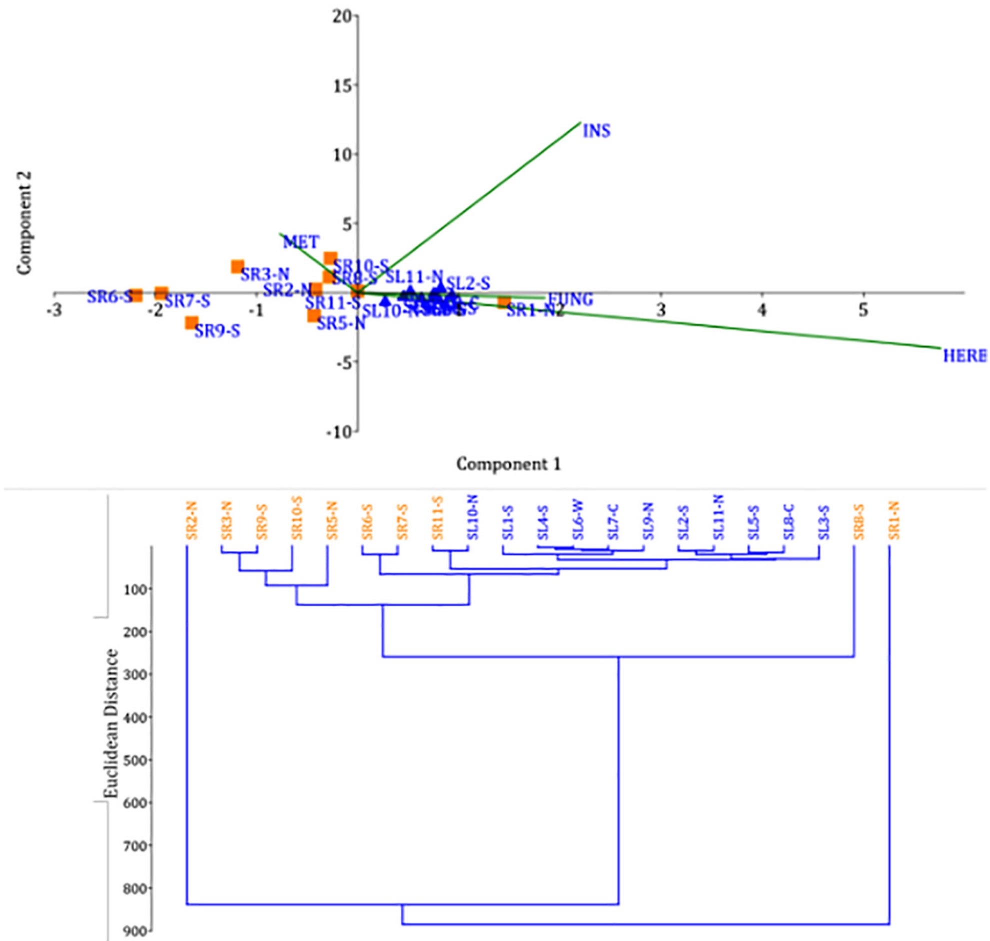



**Fig. 11.** Principal Component Analysis scatter plot and Cluster of the sediment samples of ricefields (orange) and Lake Albufera (blue). The legend labels were performed as the water samples but including the initial S to indicate sediment. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

fungicides and herbicides in the sediment were very similar in both habitats while the accumulated values calculated by area in dry weight revealed that the ricefields had eight times more pesticides (0.8 kg $ha^{-1}$) than Lake Albufera (0.1 kg $ha^{-1}$). In terms of flooded area, the rice fields reached one tonne of pesticides (1027 kg) and the lake reached 18 kg.

### 3.5. Risk assessment

The (RQ) was calculated for several organisms of the Natural Albufera Park. The mean and maximum concentrations of the pesticides were used in the calculations. The majority of pesticides that had effects in the short-term ($EC_{50}$) also did in the long-term

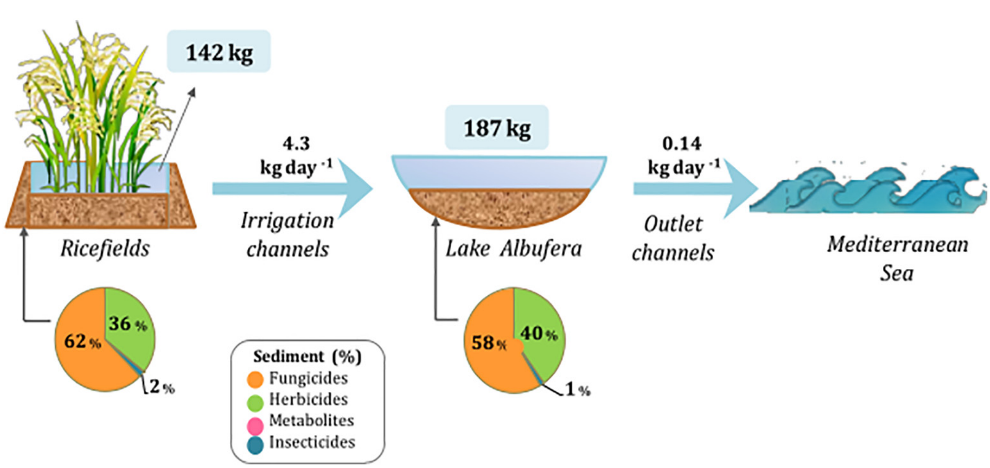



**Fig. 12.** Hydrological balance of pesticides in the water and the sediment of the aquatic habitats of The Natural Park of the Albufera in July 2016. The arrows represent the irrigation channels and the outlets and the direction of the water flow when discharged to Lake Albufera from the rice fields. The waterflow is indicated over the arrows. The output flow from the outlets is monthly mean data.

**Table 2**
Risk Quotient values obtained with $EC_{50}$ data for the primary producers present in the Natural Park of the Albufera analyzed. Mean and maximum (max.) are the pesticides concentrations of the complete cultivation period.

| Pesticides | Primary producers risk quotient ($EC_{50}$) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *Pseudokirchneriella subcapitata* | | *Scenedesmus subspicatus* | | *Chlorella* sp. | | *Anabaena flos-aquae* | | *Navicula pelliculosa* | | *Nitzschia palea* | | *Lemna* sp. | |
| | Mean | Max | Mean | Max | Mean | Max | Mean | Max | Mean | Max | Mean | Max | Mean | Max |
| Bensulfuron methyl | >1 | >1 | | | | | >1 | >1 | 0.2 | 0.8 | >1 | >>1 | >>1 | >1 |
| Bentazone | 0.9 | <1 | | | | | 0.4 | >1 | | | | | 0.8 | >1 |
| MCPA | | >1 | | | | | 0.02 | 0.1 | 0.9 | >1 | | | 0.5 | 1.0 |
| Diuron | >1 | >1 | >1 | >1 | 0.5 | 1.0 | | | 0.9 | >1 | 0.2 | 0.4 | 0.9 | >1 |
| Propanil | | >1 | | | | | 0.1 | 0.5 | >1 | >>1 | | | 0.1 | 0.5 |
| Terbutryn | >1 | >1 | | | | | | | | | | | | |
| Terbuthylazine-desethyl | | | | | | | 0.1 | 0.2 | | | | | | |
| Terbuthylazine-2-hydroxy | | | | | | | 0.1 | 0.2 | | | | | | |
| Imazalil | 0.03 | 0.2 | | | | | | | | | | | 0.1 | 0.5 |
| Prochloraz | | | >>1 | >>1 | | | | | | | | | >1 | >>1 |
| Propiconazole | >1 | >>1 | | | | | | | | | | | | |
| Tebuconazole | 0.1 | 0.6 | 0.1 | 0.6 | | | | | | | | | >1 | >1 |
| Tricyclazole | 0.2 | >1 | nd | nd | | | | | | | | | | |

>>1: RQ values one magnitude higher; "nd": no $EC_{50}$, NOEC data found.

(NOEC). This is why the results of the RQ calculated with the $EC_{50}$ were considered representative to present in the study (Tables 2 and 3). RQ values from 0.1 to 1 (medium and harmful effects, respectively) are presented for the primary producers in Table 2 and for the remaining organisms in Table 3. Only for the macroinvertebrates *Chironomus riparius* and *Eisenia fetida* is the RQ data shown with NOEC because several pesticides indicated effects at long-term instead of at short-term.

The herbicide results pointed to harmful effects (RQ > 1) for only the primary producers and the insecticides for crustaceans and *Chironomus riparius*. The fungicides result in the same negative effects for the majority of the organisms evaluated including some freshwater algae. The two metabolites of terbuthylazine supposed medium risk for cyanobacteria. The terbutryn also dropped to medium risk in chronic effects for *Pseudokirchneriella subcapitata*. The insecticides diazinon and ethion could be very dangerous for crustacean organisms such as *Daphnia* species and *Simocephalus* sp. and *Gammarus* sp. The acetamiprid and imidacloprid insecticides seemed to be particularly toxic for the macroinvertebrates *C. riparius* and *Gammarus* sp. The last one was particularly sensitive to the acetamiprid in the short and long term. The propiconazole and prochloraz had RQ values >1 for some primary producers. *Lemna* sp. was also sensitive to tebuconazole. *Daphnia magna* was also very sensitive to many fungicides in the long term (no acute or chronic data of imazalil for this cladoceran available in the databases). The propiconazole showed medium risk as chronic effect for *P. clarkii* and *Eisenia fetida*. *Lepomis* sp. was the only genus of fish with sensitivity to some pesticides, particularly to tricyclazole. NOEC data of many biocides were not available for this organism. Finally, none of the sixteen pesticides analyzed presented any risk for *Anas platyrhynchos*.

## 4. Discussion

Twenty-one pesticides were in the water and sediment samples of the aquatic habitats of the Natural Park of the Albufera were found. The use of some of these detected compounds in this study was forbidden before and during 2016: diazinon by Decision, 2007/393/EC, terbumeton and its metabolite terbumeton-desethyl, terbutryn and ethion by Regulation (EC) 2076/2002; carbendazim by Regulation (EU) 540/2011 and tricyclazole by Regulation (EU) 2016/1826. Currently, imidacloprid is only approved to use in greenhouses by Regulation (EU) 2018/783 and also the pesticides propiconazole (Regulation (EU) 2018/1856) and propanil (Regulation (EU) 2019/148) have been disapproved. The last compound was under revision about its renovation or prohibition in 2016. The chemical properties of the pesticides determined (PPDB, 2020), the regulations of their

**Table 3**
Risk Quotient values obtained with EC50 for the crustacean, mollusc and fish present in the Natural Park of the Albufera analyzed. RQ values with NOEC are showed for macroinvertebrates (**). Mean and maximum (max.) are the pesticides concentrations of the complete cultivation period.

| Pesticides | Risk quotient($EC_{50}$) | | | | | | | | | | | | Risk quotient (NOEC)** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *Daphnia magna* | | *Daphnia pulex* | | *Simocephalus* sp. | | *Gammarus fasciatus* as *Gammarus* sp. | | Bivalvia | | *Lepomis macrochirus* (as *L. gibbosus*) | | *Chironomus riparius*** | | *Eisenia fetida*** | |
| | Mean | Max | Mean | Max | Mean | Max | Mean | Max | Mean | Max | Mean | Max | Mean | MaxMax | Mean | Max |
| Acetamiprid | | | 0.3 | >1 | | | 0.3 | >1 | | | | | >1 | >1 | | |
| Diazinon | >1 | >>1 | >>1 | >>1 | >1 | >1 | >>1 | >>1 | | | | | | | | |
| Ethion | >>1 | >>1 | 0.3 | 1.0 | | | 0.3 | 1.0 | | | | | | | | |
| Imidacloprid | | | | | | | | | | | | | >>1 | >>1 | | |
| Carbendazim | 0.1 | 0.6 | | | | | | | | | | | >1 | >1 | | |
| Prochloraz | 0.1 | 0.8 | | | | | | | | | | | 0.5 | >1 | | |
| Propiconazole | 0.8 | >1 | | | | | | | 0.2 | >1 | | | | | 0.3 | >1 |
| Tebuconazole | 0.1 | 0.3 | | | | | | | | | | | 0.5 | >1 | | |
| Thiabendazole | 0.2 | 0.7 | | | | | | | 0.2 | 0.6 | | | | | | |
| Tricyclazole | 0.05 | 0.6 | | | | | | | 0.05 | 0.7 | 0.7 | >1 | 0.8 | >1 | | |

>>1: RQ values one magnitude higher; "nd": no $EC_{50}$, NOEC data found.

approval and their current status about under Regulation (EU) n° 1107/2009 is indicated in the Supplementary Table S2.

### 4.1. Water samples and rice cultivation period

The Natural Park of the Albufera was host to most of the pesticide diversity and quantities of the water in the month of July when pesticide treatments were being administered. There was a change in the presence and concentrations of pesticides during the rice cultivation period studied. Since the beginning of the cultivation period the samples of the irrigation channels and the rice fields had the highest concentrations of pesticides. However, the Lake was already showing mean concentrations higher than the other ecosystems. This result could imply that these systems had pesticides before the first treatments performed for the rice cultivation in 2016. The lake seems to have a certain amount of pesticides that are not completely eliminated. The pesticides flow from the ricefields to the lake throughout the irrigation channels and then are removed to the outlets so the lake receives the pesticides from the runoff and the outlets assumed the major part of the pesticides drained until the end of the cultivation.

The rice cultivation treatments start with the use of herbicides against the weeds and only when rice plants are growing are the fungicides poured to evade or reduce the presence of plagues responsible for rice diseases. At the beginning of the pesticide treatment the water samples only had one herbicide and four fungicides so their accumulation was due to the concentrations of the fungicides already present in this term. The outlets had also more herbicides than other biocides at this moment. The herbicides are used as the first treatment and they flow through to these channels from the ricefields during the short drainage period that is generally done in June. This may explain the increasing in magnitude orders of the concentrations accumulated in July in the aquatic systems and the fact that the herbicides duplicated the maximum values of the fungicides in this term.

The ordination analyses approximated the order usually followed by the farmers of the Natural Park treating the ricefields. The first treatments are carried out in the ricefields of the south (points 8 to 11) and are the first which drain water to the lake. The water samples of the irrigation channels in these points had more quantity of pesticides than the channels of the north (Fig. 9). The ricefields of the North points 1 and 2 had the highest values of fungicides. This may indicate that these were fields where the last applications were done because the fungicides are generally the last biocides used before harvest. Previously to the harvest of the cereal in September 2016, the Agriculture Department of the Valencian government notified of an invasive grass (*Leersia oryzoides*) recently introduced in the Valencian ricefields (GVA, 2017). This fact could be related to the presence of the herbicides and their concentrations detected in the water samples of the rice fields and irrigation channels in September. The ubiquity of the abundant pesticides in Mediterranean aquatic systems from April to June has been reported (Comoretto et al., 2007; Köck et al., 2010).The bentazone and the MCPA are post emergence herbicides sprayed on dicotyledonous and monocotyledonous weeds, respectively, in this period. The first herbicide is usually sprayed five-six weeks after sowing and needs 2–3 cm of water level flooding the fields but due to the starting of the cultivation in 2016 was delayed the absence of this herbicide in July could be justified in our results. The MCPA is generally sprayed at the beginning of the tilling of the rice, which means around the end of June but it was found early in the cultivation of 2016. Both compounds are polar herbicides with high solubility and quickly photolyzed in the water but the bentazone is more persistent in the water than the MCPA (Table S2). These properties could explain the presence of the bentazone in the aquatic habitats until September as it was found in one of the main ditches that drains water into the Mediterranean Vaccarès lagoon (Comoretto et al., 2007). The MCPA and the bentazone dropped around 100–300 ng $L^{-1}$ at late July in Vaccarès lagoon but only our results of MCPA were around 100 ng $L^{-1}$ in north and south points of Lake Albufera. Our results of bentazone in the Lake Albufera contrasted in time presence and concentrations with the maximums of 9400 ng $L^{-1}$in July and 1900 ng $L^{-1}$ in September in the Vaccarès lagoon.

The bensulfuron methyl and propanil were mainly detected in July and practically disappeared in the ecosystems. Both herbicides have low half-time in water and the propanil even less than 2 days in rice fields water (Comoretto et al., 2007; Zanella et al., 2011).

The fungicides prochloraz, propiconazole, tebuconazole and tricyclazole are post emergence fungicides usually sprayed from the midterm of July until the harvest of the rice. Propiconazole and tricyclazole are currently forbidden but the tricyclazole was under review of approbation before its expiration in October 2016 (Regulation (EU) n° 2016/1826). In fact, the use of this chemical was allowed as a terrestrial and aerial treatment by the Agricultural Ministry of Spain with an exceptional authorization from 15th July to 28th October (MAPA, 2016). It could be sprayed twice in one treatment after 15–20 days of interval. The tricyclazole has high solubility, is persistent in the water and has no stability to photolysis in the water with higher partitioning to the particles of the soil (Table S2). An experimental field study Tsochatzis et al. (2013) reported that this fungicide is not really persistent in the water of the ricefields possibly due to degradation or volatilization process and its adsorption by the sediment of the fields. The mean concentrations of tricyclazole and its frequency were lower than those detected in the water samples of the ricefields by Pareja et al. (2011). As for the concentration of 21600 ng $L^{-1}$detected in the ricefield water near Overa channel (R11-S), this might be considered as an illegal dumping.Nevertheless, the punctual concentrations of tricyclazole in the Overa channel and the North point of the Lake Albufera were close to the data reported by Andreu (2008) in July 2003 so as our peak values of tebuconazole found in July and September in the lake.

Tebuconazole concentrations of 400 to 500 ng $L^{-1}$ were found in several shallow Mediterranean lakes of Castilla y León (Spain) which support our results in Lake Albufera in July (Hijosa-Valsero et al., 2016). The presence of the tricyclazole and tebuconazole in the water of ricefields before the fungicidal treatments had been seen in field experimental studies by this author. In addition, spatial variation in the Lake was observed with higher values in the south points as this author presented. The higher values of prochloraz and propiconazole were obtained only in irrigation channels in July (3400 and 2700 ng $L^{-1}$, respectively) and were higher than tebuconazole. The propiconazole was usually used before its prohibition in 2018 with prochloraz in the same commercial product for the treatment of the rice and the tebuconazole was used post-harvest in citrus crops. These three agrochemicals are used at the beginning of July and could be used until August or September depending on the strength of the *Pyricularia* disease in the year of the cultivation. The three of them had low or moderate solubility and are bioaccumulative (Table S2). It was also found that the persistence of the prochloraz and tebuconazole in water field samples do not last more than 4–5 days (Fu et al., 2016) when as pure substances they had a half-life of 5 and 1 year (Andreu et al., 2008). The prochloraz is sensitive to photolysis and hydrolysis so it may be reasonable that the concentrations dropped from July to September to a mean of 21.2 ± 3.4 ng $L^{-1}$ in the water of the four habitats. The imazalil, carbendazim and thiabendazole were detected in concentrations lower than 100 ng $L^{-1}$. These three fungicides are not used for rice cultivation but in other crops such as citrus (oranges and tangerines) and potatoes also cultivated in the Natural Park. In fact, as mentioned before, the carbendazim had already been prohibited before 2016. Moreover, the effluents of the wastewater treatment plants (WWTPs) that are treated to irrigate the fields and the water inputs from the rivers that discharge in aquatic habitats as Lake Albufera could be and additional source of pesticide residues. For example, Merel et al. (2018) reported that textiles and papers commonly found in households could be a source of carbendazim in domestic wastewater. So the detection of these agrochemicals in the samples analyzed and its concentrations may be related to these reasons.

The insecticides and the fungicides, are sprayed as a prevention or reduction/eradication tool so the period of time for the treatment could be as wide as the cultivation period. Both biocides treatment periods run approximately from April to September as the Valencian government noted the presence of invasive organisms in any location close or in the Mediterranean wetland. The acetamiprid and imidacloprid were the insecticides most detected in the water samples of July. Despite this, these compounds were barely determined in the samples of May and September. The dissipation of neonicotinoids from water has been reported tobe largely dominated by photolysis and followed by temperature (Rico et al., 2018).Both are soluble in water and low capability of bioaccumulation (Table 1) but their main differences are that the acetamiprid persist in the water less than a week but is stable under photolysis which completely the opposite with imidacloprid.

The herbicide metabolites detected were residues of the herbicide terbumeton and terbuthylazine. The metabolites are known because of their higher persistence in the water. The terbumeton is not approved but the terbuthylazine remains approved. The presence of these triazines in our samples could be due to the water inputs from Turia River to the Albufera. These compounds were determined in the water samples collected from Turia River in 2012 and 2013 (Ccanccapa et al., 2016). Their median and occurrence data of the metabolites were quite in concordance with our statistical data.

Our concentrations of the herbicides diuron, terbutryn and the terbuthylazine metabolites classified as priority substances in annex X Directive, 2000/60/EEC did not trespass the maximum concentrations established in the annex II of the Directive, 2013/39/EU for continental surface waters. It has been observed in this study that the pesticides concentrations of the water samples analyzed surpassed the maximum individual (100 ng $L^{-1}$) and total concentrations (500 ng $L^{-1}$) allowed by the legislation of European Union for groundwater (Directive 2006/118/EEC) and drinking water (Directive 98/83/EEC).

### 4.2. Sediment samples

The pesticides detected and identified in the sediment samples were no different to those in the water samples but four of them were not found, such as MCPA, terbumeton, terbutryn and terbuthylazine-desethyl. The same dominant pesticides as in the water samples were also found. The higher persistence of the tricyclazole in sediment has been settled in paddy experimental and field studies of dissipation (Tsochatzis et al., 2013) under different moisture, pH, and other field conditions (Kumar et al., 2017). The other fungicides are less mobile to the sediment so the concentrations lower than 100 ng $g^{-1}$ d.w. could be explained by this property. The fact that these compounds were found in Lake Albufera in even smaller concentrations than the fields may be because they were dragged with suspended solids from the rice fields and the water inputs from the Turia and Júcar rivers. The sediment of several inland wetlands in Spain (Hijosa-Valsero et al., 2016) and various restored wetlands in agricultural landscapes in Iowa, USA (Smalling et al., 2015) did not detect tebuconazole which is in contrast with our results. The bentazone was suggested to percolate the soils in order to reach the surface and groundwater in different soils from marches surrounding The Doñana National Park (Romero et al., 1996). The mobility of both dominant pesticides from water to sediment and the information reported supports our results of their presence in the sediment of both systems. The biodegradation of bensulfuron methyl with actinomycetes, fungi and bacteria by oxidation and hydrolysis was observed in a field study in California (Mabury and Crosby, 1996). This study also reported that the bensulfuron methyl had a fast degradation at higher pH in soil and that the MCPA proceeded at the greatest rate of degradation in soils under moderate moisture. However, a three-year field experiment conducted in Spain under aerobic and anaerobic rice crop conditions mentioned that aerobic conditions and lower values of pH in soil were greater than the sorption of both herbicides while bensulfuron methyl needs higher content of humic acids and MCPA fulvic acids (López-Piñeiro et al., 2019). These reasons could explain the low rate and absence in the sediment samples of the bensulfuron methyl and the MCPA. Acetamiprid and imidacloprid have been detected in sediment of vegetable planting areas in South China where and the imidacloprid dominated the neonicotinoid composition of rice areas (Huang et al., 2020).This study might corroborate the detection of imidacloprid in our ricefield sediment samples and not in the lake although the occurrence was higher for the acetamiprid in the ricefields.

The pairs or groups strongly correlated in the correlation analyses were imazalil with tebuconazole, prochloraz with tebuconazole and bentazone with prochloraz and tricyclazole. These correlations might be related to the composition of the commercial pesticide products. Some of the products are formulated by one active substance or are a mix of two active substances such as “Teycer” products manufactured in Valencia (Spain) (MAPA, 2020). Both of these last groups also coincide with the correlations of the water samples of July. The clustering of the compounds suggested a relationship with cultivations treatments. The first pair of fungicides are not used in rice but in citrus crops. The prochloraz and the tebuconazole are used around the same period of time starting in July and are combined depending on the time of the appearance of the rice diseases. The tebuconazole has a broader spectrum of rice diseases to be used. The last group is formed by the dominant pesticides bentazone and tricyclazole and both are correlated to the prochloraz. No similar time of treatment or chemical properties could suggest this relationship.

### 4.3. Risk assessment

The Risk Quotient results range from RQ > 1 which means harmful effects could be expected due to the pesticide in water to RQ < 0.1 that involves a low environmental risk. RQ values between 0.1 and 1 which means medium risk. Our main results were mainly focused on the RQ values >1. Some of the $EC_{50}$ and NOEC data was not available in the databases explored so it was not possible to calculate the risk quotient of many pesticides for the studied organisms of the Mediterranean wetland.

The higher sensitivity to growth rate algae species to herbicides was already reported (Sabater et al., 2002; Tarazona et al., 2003). It was mentioned that *Scenedesmus* species (*S. acutus* and *S. subspicatus*) were more sensitive than *Chlorella* species to bensulfuron methyl. The author also reported the sensitivity of *Scenedesmus* species and cyanobacteria *Pseudanabaena galeata* to an insecticide of the same chemical group (organophosphorus) than our detected diazinon and ethion. Suárez-Serrano et al., 2010 indicated negative effects from herbicides and fungicides in phytoplanktonic organisms as the microalgae studied and *D. magna* from the ricefield waters.

Our results of the neonicotinoids are in accordance to Rico et al. (2018) that found genus *Chironomini* as the most sensitive of the macroinvertebrates analyzed to the imidacloprid.

Some toxicological studies may support our results of the risk of some fungicides to the algae community. It has been observed that *Navicula* species were inhibited by carbendazim in 24 h and despite the recovery of the algal growth, the chlorophyll-a content remained significantly decreased at 0.5 mg $L^{-1}$ of this fungicide (Ding et al., 2019). Laboratory experiments of the dissipation of carbendazim and prochloraz in monoalgae cultures showed that *Scenedesmus acutus* and *S. subspicatus* were more efficient than *Chlorella* sp. in the elimination of these fungicide concentrations (Andreu et al. 2008). The fact that the propiconazole could be harmful to *Eisenia fetida* could supplement the reported information by Rico et al. (2016) about the earthworm sensitivity to fungicides. The author found that the carbendazim was highly toxic in only a short period to this organism. The study of Wandscheer et al. (2017) indicated that tebuconazole and tricyclazole single dose did not make significant effects in the macroinvertebrate richness and density but precisely due to the high persistence of both fungicides in the water of the ricefields, recommended careful control of the dosage and number of applications to avoid environmental contamination.

## 5. Conclusions

The Natural Park of the Albufera supports large amounts of several pesticides during rice cultivation. The water and the sediment samples had common pesticides, most of them from rice cultivation and othersfrom the treatment of other crops. The most ubiquitous and dominant pesticides found in the water and sediment of the aquatic systems were the bentazone and the tricyclazole. Some of the agrochemicals determined pose a risk to the aquatic and terrestrial organisms of the Natural Park. The high values obtained in the risk assessment of this predicted negative effects on the biota. Our results suggested that the phytoplankton species of the wetland were highly sensitive to the herbicides and fungicides. The fungicides were also found to have an important impact on many of the taxa analyzed of the biota studied. Further studies about the environmental behaviour of the agrochemicals broadly used in rice cultivation as well as their toxicity on the native organisms of this wetland are recommended.

Although the pesticides authorized for rice plant treatment could change from one year to another and the variations in the climate conditions with the inputs/outputs of the water flow between ecosystems can also influence the length of the cultivation period a, our estimations gave an idea of the magnitude of the quantity of pesticides that the rice cultivationsupplies in a year. The concentrations obtained in the real water volume and flooded area were estimated in hundreds of kilograms in the ricefields and Lake Albufera during 2016.These approximated quantities should be considered as a warning about the possible impact on the organisms and habitats of Mediterranean ecosystems subjugated to agricultural pressure like the Natural Park of the Albufera.

## Declaration of competing interest

None.

## Acknowledgements

The research that led to these results received funding from the-Spanish Ministry of Science, Innovation and Universities and the European Regional Development Fund through the project WETANDPAC (RTI2018-097158-B-C31) and from the Generalitat Valenciana through the project ANTROPOCEN@ (PROMETEO/2018/155).

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.145009.

## References

Alonso, J.L., Sabater, C., Ibáñez, M.J., Amorós, I., Botella, M.S., Carrasco, J., 1997. Fenitothrion and 3-methyl-4-nitrophenol degradation by two bacteria in natural waters under laboratory conditions. J. Environ. Sci. Health. A32 (3), 799–812.

Amoros, I., Connon, R., Garelick, H., Alonso, J.L., Carrasco, J.M., 2000. An assessment of the toxicity of some pesticides and their metabolites affecting a natural aquatic environment using the Microtox (TM) system. Water Sci. Technol. 42, 19–24.

Andreu, O., 2008. Evaluación de riesgosambientales del uso de plaguicidasempleadosen el cultivo del arroz en el Parque Natural de La Albufera de Valencia. Universitat Politècnica de València, Doctoral Thesis.

Antón-Garrido, B., Romo, S., Villena, M.J., 2013. Diatom species composition and indices for determining the ecological status of coastal Mediterranean Spanish lakes. AnalesJard. Bot. Madrid 70 (2), 122–135. https://doi.org/10.3989/ajbm.2373.

APHA, 2011. Standard Methods for the Examination Water and Wastewater. 22nd ed. American Public Health Association, Washington D.C.

Blanco, S., Romo, S., 2006. Ictiofauna del Lago de la Albufera de Valencia: Evoluciónhistórica y situación actual. Bol. R. Soc. Esp. Hist. Nat. (Sec. Biol.), 101 (1-4), 45-56.

Blanco, S., Romo, S., Villena, M.J., Martínez, S., 2003. Fish communities and food web interactions in some shallow Mediterranean lakes. Hydrobiologia 506–509, 473–480.

Boluda, R., Quintanilla, J.F., Bonilla, J.A., Sáez, E., Gamón, M., 2002. Application of the Microtox® test and pollution indices to the study of water toxicity in the Albufera Natural Park (Valencia, Spain). Chemosphere 46 (2), 355–369. https://doi.org/10.1016/S0045-6535(01)00092-3.

Boluda, R., Marimon, L., Atzeni, S., Mormeneo, S., Iranzo, M., Zueco, J., Gamón, M., Sancenón, J., Romera, D., Gil, C., Soriano, M.A., Granell, C., Roca, N. Bech, J., 2013. Occurrence of emerging contaminants in agricultural soils, sewage sludge and waters in Valencia (E Spain). GeophysicalResearchAbstracts 15, EGU2013-7998. EGU General Assembly 2013.

Burillo, L., 1999. Diversidad y calidadbiológicas de las aguas del Parque Natural de l'Albufera (Valencia). Doctoral Thesis. Universitat de València.

Calatayud-Vernich, P., Calatayud, F., Simó, E., Picó, Y., 2019. A two-year monitoring of pesticide hazard in-hive: high honey bee mortality rates during insecticide poisoning episodes in apiaries located near agricultural settings. Chemosphere 232, 471–480. https://doi.org/10.1016/j.chemosphere.2019.05.170.

Carmona, E., Andreu, V., Picó, Y., 2017. Multi-residue determination of 47 organic compounds in water, soil, sediment and fish—Turia River as case study. J. Pharm. Biomed. Anal. 146, 117-125. doi:doi:https://doi.org/10.1016/j.jpba.2017.08.014.

Carrasco, J.M., Planta, M., 1985. Contaminación de la Albufera de Valencia por plaguicidasutilizadosen el cultivo del arroz. Rev. Agroquím. Tecnol. Aliment. 25 (1), 144–148.

Carrasco, J.M., Cuñat, P., Martínez, R.M., Primo, E., 1972. Contaminación de la Albufera de Valencia por plaguicidas. I. Niveles de contaminación por insecticidas. Rev. Agroquím. Tecnol. Aliment. 12, 583–596.

Castillo, M.A., Aragon, P., Sabater, C., 2003. Herbicide residues in irrigation well water in a citrus area of Spain. Pesticide in Air, Plant, Soil and Water System. Proc. XII Symposium on Pesticide Chemistry, Piacenza, Italy, pp. 915–921.

Ccanccapa, A., Masiá, A., Andreu, V., Picó, Y., 2016. Spatio-temporal patterns of pesticide residues in the Turia and Júcar rivers (Spain). Sci. Total Environ. 540, 200–210.

Comoretto, L., Arfib, B., Chiron, S., 2007. Pesticides in the Rhône river delta (France): basic data for a field-based exposure assessment. Sci. Total Environ. 380, 124–132. doi:doi:10.1016/j.scitotenv.2006.11.046.

Directive 92/43/EEC of 21 May 1992 on the conservation of natural habitats and of wild fauna and flora.

Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption.

Decision 2007/393/EC of 6 June 2007concerning the non-inclusion of diazinon in Annex I to Council Directive 91/414/EEC and the withdrawal of authorisations for plant protection products containing that substance.

Ding, T., Li, W., Li, J., 2019. Toxicity and metabolic fate of the fungicide carbendazim in the typical freshwater diatom navicula species. J. Agric. Food Chem. 67, 6683–6690. https://doi.org/10.1021/acs.jafc.8b06179.

Directive 2000/60/EC of the European parliament and of the council of 23 October 2000 establishing a framework for Community action in the field of water policy.

Directive 2006/11/EC of the European parliament and of the council of 15 February 2006 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community.

Directive 2006/118/EC of the European parliament and of the council of 12 December 2006 on the protection of groundwater against pollution and deterioration.

Directive 2009/147/EC of the European parliament and of the council of 30 November 2009 on the conservation of wild birds.

Directive 2009/128/EC of the European parliament and of the council of 21 October 2009 establishing a framework for Community action to achieve the sustainable use of pesticides.

Directive 2013/39/EU of the European parliament and of the council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy.

European Commission, 2003. Technical guidance document on risk assessment in support of Commission Directive 93/67/EEC on risk assessment for new notified substances, Commission Regulation (EC) No 1488/94 on risk assessment for existing substances, and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market. Part II: Environmental Risk Assessment. Office for Official Publications of the European Communities, Luxembourg. 2003.

European Commission, 2020. Food Safety. Plants. Pesticides. https://ec.europa.eu/food/plant/pesticides_en.

Fu, Y., Zheng, Z., Wei, P., Wang, M., Zhu, G., Liu, Y., 2016. Distribution of thifluzamide, fenoxanil and tebuconazole in rice paddy and dietary risk assessment. Toxicol. Environ. Chem. 98, 118–127. https://doi.org/10.1080/02772248.2015.1113288.

Gamón, M., Boluda, R., Gómez de Barreda, E., Sáez, E., Gil, J., García de la Cuadra, J., Ten, A., Lleeó de Otai, C., Lorezo, E., Pelegrí, R., Aliaga, T., Sáez, A., 2002. Evaluación de plaguicidasen los canales de riego del Parque Natural de la Albufera de Valencia. In: Agüera, A., Rodríguez, A. (Eds.), Evaluación y seguimiento de plaguicidasenaguassubterráneas y superficiales. Universidad de Almería, pp. 25–56.

Gamón, M., Sáez, E., Gil, J., Boluda, R., 2003. Direct and indirect exogenous contamination by pesticides of rice-farming soils in a Mediterranean wetland. Arch. Environ. Contam. Toxicol. 44, 141–151. https://doi.org/10.1007/s00244-002-2008-3.

Gómez de Barreda, D., 1999. Comportamiento de herbicidasresidualesensuelos. Universitat Politècnica de València, Posiblecontaminación de acuíferos. Doctoral Thesis.

GVA, 2017. Generalitat Valenciana. Publicaciones y estadísticas. Agricultura y Desarrollo Rural. Boletín de avisos https://www.agroambient.gva.es/es/boletin-de-avisos accessed 13 November 2017.

Hammer, Ø., Harper, D.A.T., Ryan, P.D., 2001. PAST: paleontological statistics software package for education and data analysis. Palaeontol. Electron. 4(1), 9pp.

Hijosa-Valsero, M., Bécares, E., Fernández-Aláez, C., Fernández-Aláez, M., Mayo, R., Jiménez, J.J., 2016. Chemical pollution in inland shallow lakes in the Mediterranean

region (NW Spain): PAHs, insecticides and herbicides in water and sediments. Sci. Total Environ. 544, 797–810. https://doi.org/10.1016/j.scitotenv.2015.11.160.
Huang, Z., Li, H., Wei, Y., Xiong, J., You, J., 2020. Distribution and ecological risk of neonicotinoid insecticides in sediment in South China: Impact of regional characteristics and chemical properties. Sci. Total Environ. 714, 136878. doi:doi:https://doi.org/10.1016/j.scitotenv.2020.136878.
Köck, M., Farré, M., Martínez, E., Gajda-Schrantz, K., Ginebreda, A., Navarro, A., de Alda, M.L., Barceló, D., 2010. Integrated ecotoxicological and chemical approach for the assessment of pesticide pollution in the Ebro River delta (Spain). J. Hydrol. 383, 73–82. doi:doi:https://doi.org/10.1016/j.jhydrol.2009.12.029.
Kumar, N., Mukherjee, I., Sarkar, B., Paul, R.K., 2017. Degradation of tricyclazole: effect of moisture, soil type, elevated carbon dioxide and Blue Green Algae (BGA). J. Hazard. Mater. 321, 517–527. https://doi.org/10.1016/j.jhazmat.2016.08.073.
López-Piñeiro, A., Peña, D., Albarrán, Á., Sánchez-Llerena, J., Becerra, D., Fernández, D., Gómez, S., 2019. Environmental fate of bensulfuron-methyl and MCPA in aerobic and anaerobic rice-cropping systems. J. Environ. Manage. 237, 44–53. https://doi.org/10.1016/j.jenvman.2019.02.058.
Mabury, S.A., Cox, J.S, Crosby, D.G., 1996. Environmental fate of rice pesticides in California. Rev. Environ. Contam. Toxicol.147:71-117. doi:https://doi.org/10.1007/978-1-4612-4058-7_3.
MAPA, 2016. Resolución de autorizaciónexcepcional para la aplicación por métodosaéreos y terrestres de productosfitosanitarios a base de Triciclazol 75% P/P [WP] contra Piricularia (Pyriculariaoryzae) en arroz. Ministerio de Agricultura, Alimentación y Medioambiente. https://www.juntadeandalucia.es/export/drupaljda/RESOLUCION%20TRICICLAZOL%20PIRICULARIA%20ARROZ.pdf accessed 9 November 2017.
MAPA, 2020. Ministerio de Agricultura, Pesca y Alimentación. Medios de defensa sanitaria, Registro de Productos Fitosanitarios https://www.mapa.gob.es/es/agricultura/temas/sanidad-vegetal/productos-fitosanitarios/registro/menu.asp accessed 27 February 2020.
Masiá, A., Vásquez, K., Campo, J., Picó, Y., 2015. Assessment of two extraction methods to determine pesticides in soils, sediments and sludges. Application to the Túria River Basin. J. Chromatogr. A 1378, 19–31. https://doi.org/10.1016/j.chroma.2014.11.079.
Merel, S., Benzing, S., Gleiser, C., Di Napoli-Davis, G., Zwiener, C., 2018. Occurrence and overlooked sources of the biocide carbendazim in wastewater and surface water. Environ. Pollut. 239, 512–521. https://doi.org/10.1016/j.envpol.2018.04.040.
Olmo, C., 2016. Zooplankton Assemblages in a Mediterranean Restored Area: Patterns and Processes of Colonization and Establishment. Doctoral thesis. Universitat de València.
Onandia, G., Gudimov, A., Miracle, M.R., Arhonditsis, G., 2015. Towards the development of a biogeochemical model for addressing the eutrophication problems in the shallow hypertrophic lagoon of Albufera de Valencia, Spain. Ecol. Inform. 26, 70–89. https://doi.org/10.1016/j.ecoinf.2015.01.004.
OPP Pesticide Ecotoxicity Database, 2020. United States Environmental Protection Agency (USEPA). https://ecotox.ipmcenters.org/index.cfm?menuid=5 accessed 13 February 2020.
Pareja, L., Martínez-Bueno, M.J., Cesio, V., Heinzen, H., Fernández-Alba, A.R., 2011. Trace analysis of pesticides in paddy field water by direct injection using liquid chromatography-quadrupole-linear ion trap-mass spectrometry. J. Chromatogr. A 1218, 4790–4798. https://doi.org/10.1016/j.chroma.2011.02.044.
Peris, E., Requena, S., De La Guardia, M., Pastor, A., Carrasco, J.M., 2005. Organochlorinated pesticides in sediments from the Lake Albufera of Valencia (Spain). Chemosphere 60, 1542–1549. https://doi.org/10.1016/j.chemosphere.2005.02.043.
PPDB, 2020. Pesticide Properties DataBase. University of Hertfordshire https://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm accessed 14 April 2020.
Ramsar, 2016. An Introduction to the Ramsar Convention on Wetlands, 7th ed. (previously The Ramsar Convention Manual). Ramsar Convention Secretariat, Gland, Switzerland.
Real Decreto 1311/2012, de 14 de septiembre, por el que se establece el marco de actuación para conseguir un usosostenible de los productosfitosanitarios. BOE-A-2012-11605.
Regulation (EC) 2076/2002 of 20 November 2002 extending the time period referred to in Article 8(2) of Council Directive 91/414/EEC and concerning the non-inclusion of certain active substances in Annex I to that Directive and the withdrawal of authorisations for plant protection products containing these substances.
Regulation (EC)nº 1107/2009 of the European parliament and of the council of 21October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC Regulation (CE) 1107/2009.
Regulation (EU) 2016/1826 of 14 October 2016 concerning the non-approval of the active substance tricyclazole, in accordance with Regulation (EC) No 1107/2009 of the European Parliament and of the Council concerning the placing of plant protection products on the market.
Regulation (EU) 2018/783 of 29 May 2018 amending implementing Regulation (EU) No 540/2011 as regards the conditions of approval of the active substance imidacloprid.
Regulation (EU) 2018/1856 of 28 November 2018 concerning the non-renewal of approval of the active substance propiconazole, in accordance with Regulation (EC) Nº 1107/2009 of the European Parliament and of the Council concerning the placing of plant protection products on the market, and amending Commission Implementing Regulation (EU) Nº 540/2011.
Regulation (EU) 2019/148 of 30 January 2019 concerning the non-approval of the active substance propanil, in accordance with Regulation (EC) No 1107/2009 of the European Parliament and of the Council concerning the placing of plant protection products on the market.
Regulation (EU) nº540/2011 of 25 May 2011 implementing Regulation (EC) No 1107/2009 of the European Parliament and of the Council as regards the list of approved active substances.
Resolución n° 2008/1202. Resolución 17 de enero de 2008, del director general de Investigación y TecnologíaAgroalimentaria, por la que se establecen las normas para la producciónintegradaen arroz, en el ámbito de la ComunitatValenciana. [2008/1202]. DOCV n° 5696/05.02.2008. pp: 5493–5507.
Rico, A., Sabater, C., Castillo, M.-Á., 2016. Lethal and sub-lethal effects of five pesticides used in rice farming on the earthworm *Eisenia fetida*. Ecotoxicol. Environ. Saf. 127, 222–229. https://doi.org/10.1016/j.ecoenv.2016.02.004.
Rico, A., Arenas-Sánchez, A., Pasqualini, J., García-Astillero, A., Cherta, L., Nozal, L., Vighi, M., 2018. Effectsof imidacloprid and a neonicotinoid mixture onaquaticinvertebratecommunitiesunderMediterraneanconditions. Aquat. Toxicol. 204, 130–143. https://doi.org/10.1016/j.aquatox.2018.09.004.
Romero, E., Sánchez-Rasero, F., Pena, A., de laColina, C., Dios, G., 1996. Bentazone leaching in Spanish soils. Pestic. Sci. 47 (1), 7–15.
Romo, S., van Tongeren, O., 1995. Multivariate analysis of phytoplankton and related environmental factors, in a shallow hypertrophic lake. Hydrobiologia 299, 93–101. https://doi.org/10.1007/BF00017561.
Romo, S., Villena, M.J., Sahuquillo, M., Soria, J.M., Giménez, M., Alfonso, T., Vicente, E., Miracle, M.R., 2005. Response of a shallow Mediterranean lake to nutrient diversion: does it follow similar patterns as in northern shallow lakes? FreshwaterBiology 50, 1706–1717. https://doi.org/10.1111/j.1365-2427.2005.01432.x.
Romo, S., García-Murcia, A., Villena, M.J., Sánchez, V., Ballester, A., 2008. Tendencias del fitoplanctonen el lago de la Albufera de Valencia e implicaciones para suecologíagestión y recuperación. Limnética 27 (1), 11–28. https://doi.org/10.23818/limn.27.02.
Romo, S., Soria, J., Fernandez, F., Ouahid, Y., Barón-Solá, Á., 2013. Water residence time and the dynamics of toxiccyanobacteria. FreshwaterBiology 58 (3), 513–522. https://doi.org/10.1111/j.1365-2427.2012.02734.x.
Rueda, J., López, C., Hernández, R., 2005. Evaluación de la calidad de los ecosistemasacuáticos a partir del modo de nutrición (IMN) de sus macroinvertebrados. Una adaptación para la educaciónsecundaria. Didáctica de las CienciasExperimentales y Sociales 19, 103–114. https://ojs.uv.es/index.php/dces/article/view/2442.
Rueda, J., Aguilar-Alberola, J., Mesquita-Joanes, F., 2006. Contribución al conocimiento de los crustáceos (Arthropoda, Crustacea) de las Malladas de la Devesa del Parque Natural de la Albufera (Valencia). Boletín la Asoc. Española Entomol. 30 (1–2), 9–29.
Sabater, C., Carrasco, J.M., 1996. Effects of thiobencarb on growth of three freshwater species of phytoplankton. Bull. Environ. Contam. Toxicol. 56, 977–984.
Sabater, C., Carrasco, J.M., 1997. Effects of chlorsulfuron on growth of three freshwater species of phytoplankton. Bull. Environ. Contam. Toxicol. 58, 807–813.
Sabater, C., Carrasco, J.M., 1998. Effects of molinate on growth of five freshwater species of phytoplankton. Bull. Environ. Contam. Toxicol. 6, 534–540.
Sabater, C., Carrasco, J.M., 2001. Effects of the organophosphorus insecticide Fenitrothion on growth of five freshwater species of phytoplankton. EnvironToxicol. 16 (4), 314–320. https://doi.org/10.1002/tox.1038.
Sabater, C., Cuesta, A., Carrasco, R., 2002. Effects of bensulfuron-methyl and cinosulfuron on growth of four freshwater species of phytoplankton. Chemosphere 46, 953–960. https://doi.org/10.1016/S0045-6535(01)00179-5.
Smalling, K.L., Reeves, R., Muths, E., Vandever, M., Battaglin, W.A., Hladik, M.L., Pierce, C.L., 2015. Pesticide concentrations in frog tissue and wetland habitats in a landscape dominated by agriculture. Sci. Total Environ. 502, 80–90. doi:doi:10.1016/j.scitotenv.2014.08.114.
Soria, J.M., Romo, S., Aledón, T., Izquierdo, J.F., Calvo, S., Pastor, A., García, A., Arribas, I., 2015. Estudio de la inundaciónotoñalen el Parque Natural de la Albufera de Valencia medianteimágenes de Landsat. XVI Congreso de la Asociación Española de Teledetección, Sevilla 21-23, 370–373.
Suárez-Serrano, A., Ibáñez, C., Lacorte, S., Barata, C., 2010. Ecotoxicological effects of rice field waters on selected planktonic species: comparison between conventional and organic farming. Ecotoxicology (London, England) 19 (8), 1523–1535. https://doi.org/10.1007/s10646-010-0537-5.
Tarazona, C., 2001. Evolucióestacional de la contaminació de l'Albufera de Vàlenciaiefectesobre les poblacionsfitoplanctòniques. Anàlisi de riscambiental per l'ús de plaguicides. Doctoral Thesis. Universitat Politècnica de València.
Tarazona, C., Carrasco, J.M., Sabater, C., 2003. Monitoring of rice pesticides in an aquatic system of Natural Park of Albufera, Valencia, Spain. Pesticide in Air, Plant, Soil and Water System. Hazard Evaluation. Proc. XII Symposium on Pesticide Chemistry, Piacenza, Italy. 4-6, pp. 727–735.
Tsochatzis, E.D., Tzimou-Tsitouridou, R., Menkissoglu-Spiroudi, U., Karpouzas, D.G., Katsantonis, D., 2013. Laboratory and field dissipation of penoxsulam, tricyclazole and profoxydim in rice paddy systems. Chemosphere 91, 1049–1057. https://doi.org/10.1016/j.chemosphere.2013.01.067.
USGS, 2018. Earth Explorer United States Geological Survey. https://earthexplorer.usgs.gov/(accessed 10 December 2018).
Vázquez-Roig, P., Blasco, C., Andreu Pérez, V., Picó, Y., 2010. Assessment of pesticide contamination in soil and water samples from Natural Park of L'Albufera using liquid chromatography tandem mass spectrometry. 28th International symposium on chromatography.
Villena, M.J., Romo, S., 2003. 2003. Phytoplankton changes in a shallow Mediterranean lake (Albufera of Valencia, Spain) after sewage diversion. Hydrobiologia 506, 281–287. https://doi.org/10.1023/B:HYDR.0000008565.23626.aa.
Wandscheer, A., Marchesan, E., Santos, S., Zanella, R., Silva, M.F., Londero, G.P., Donato, G., 2017. Richness and density of aquatic benthic macroinvertebrates after exposure to fungicides and insecticides in rice paddy fields. Anais da Academia Brasileira de Ciencias 89 (1), 355–369. https://doi.org/10.1590/0001-3765201720160574.
Zanella, R., Adaime, M.B., Peixoto, S.C., do A. Friggi, C., Prestes, O.D., Machado, S.L.O., Marchesan, E., Avila, L.A., Primel, E.G., 2011. Herbicides persistence in Rice Paddy water in Southern Brazil. In: Hasaneen, M.N.A.E.-G. (Ed.), Herbicides. IntechOpen, Rijeka https://doi.org/10.5772/32727.