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Influence of climate change and pesticide use practices on the ecological risks of pesticides in a protected Mediterranean wetland: A Bayesian network approach

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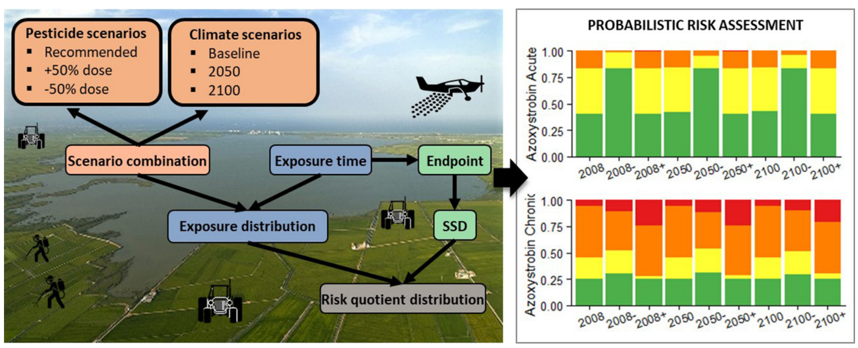
HIGHLIGHTS

- The ecological risks of 9 pesticides were assessed using Bayesian networks.
- Bayesian networks allow the integration of climate change and pesticide use scenarios.
- Local precipitation is more important than temperature raise for pesticide exposure.
- Azoxystrobin, difenoconazole and MCPA show high ecological risks.
- The 'Farm-to-Fork' strategy needs complementary measures to eliminate risks.

GRAPHICAL ABSTRACT



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ABSTRACT

Pollution by agricultural pesticides is one of the most important pressures affecting Mediterranean coastal wetlands. Pesticide risks are expected to be influenced by climate change, which will result in an increase of temperatures and a decrease in annual precipitation. On the other hand, pesticide dosages are expected to change given the increase in pest resistance and the implementation of environmental policies like the European ´Farm-to-Fork` strategy, which aims for a 50 % reduction in pesticide usage by 2030. The influence of climate change and pesticide use practices on the ecological risks of pesticides needs to be evaluated making use of realistic environmental scenarios. This study investigates how different climate change and pesticide use practices affect the ecological risks of pesticides in the Albufera Natural Park (Valencia, Spain), a protected Mediterranean coastal wetland. We performed a probabilistic risk assessment for nine pesticides applied in rice production using three climatic scenarios (for the years 2008, 2050 and 2100), three pesticide dosage regimes (the recommended dose, and 50 % increase and 50 % decrease), and their combinations. The scenarios were used to simulate pesticide exposure concentrations in the water column of the rice paddies using the RICEWQ model. Pesticide effects were characterized using acute and chronic Species Sensitivity Distributions built with toxicity data for aquatic organisms. Risk quotients were calculated as probability distributions making use of Bayesian networks. Our results show that future climate projections will influence exposure concentrations for some of the studied pesticides, yielding higher dissipation and lower exposure in scenarios dominated by an increase of temperatures, and higher exposure peaks in scenarios where heavy precipitation events occur right after

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pesticide application. Our case study shows that pesticides such as azoxystrobin, difenoconazole and MCPA are posing unacceptable ecological risks for aquatic organisms, and that the implementation of the ´Farm-to-Fork` strategy is crucial to reduce them.

1. Introduction

Mediterranean coastal wetlands have been considered biodiversity hotspots and play an important role in ecosystem service provision (Pérez-Ruzafa and Marcos, 2008). Several studies show that these ecosystems are impacted by a wide range of anthropogenic stressors (Martínez-Megías and Rico, 2022; Newton et al., 2014). Pollution by agricultural pesticides is one of the most important ones (Barbieri et al., 2020; Barhoumi et al., 2014; Calvo et al., 2021; Ccanccapa et al., 2016), however their impacts on aquatic ecosystem structure and biodiversity have been seldom investigated (Martínez-Megías and Rico, 2022). Some studies report that the presence of pesticides can have significant effects on aquatic communities (Pitacco et al., 2020), affecting food web stability and the relative abundance of predator and prey species (Quintana et al., 2018). Also, pesticide risks could significantly vary over time, becoming critical in some periods of the year due to interactions with other natural or anthropogenic stressors related to global climate change (Duchet et al., 2010).

The last report by the Intergovernmental Panel on Climate Change has predicted a temperature increase of up to 5.6 degrees for the Mediterranean region by the end of 21st century, which is accompanied by a decrease in annual precipitations and an increasing occurrence of extreme events such as severe droughts and heatwaves (Ali et al., 2022). Although some authors have found that climate change could notably influence the environmental fate and toxicity of pesticides (Arenas-Sánchez et al., 2019; Holmstrup et al., 2010; Vilas-Boas et al., 2021), others indicate lower side-effects in water bodies due to increasing biodegradation (Willming and Maul, 2016). Thus, there is no apparent consensus on whether climate change is expected to increase or decrease pesticide risks for aquatic ecosystems.

The beneficial effect of warming on pesticide dissipation rates could be offset by an increase in the occurrence of agricultural pests. In fact, several studies show that under a climate change scenario some agricultural pests could spread beyond their original distribution areas (Eitzinger et al., 2013) and become more prevalent in a higher number of agricultural crops (Noyes et al., 2009). Therefore, it is expected that many farmers tend to increase pesticide dosages per cropland area in regions with a significant increase in temperatures or precipitation (Delcour et al., 2015; Hader et al., 2022). This is supported by the fact that, despite legal restrictions have been put in place in many regions of Europe, this has not been translated into a reduction on the total amount of pesticides used in agriculture (Lamichhane et al., 2016).

On the other hand, the continued reliance on agricultural pesticides and their environmental impacts has been addressed through the enactment of the European Green Deal by the European Commission. This policy includes the ´Farm-to-Fork` strategy, which aims for a 50 % reduction in pesticide usage by 2030 (European Commission, 2021). Therefore, it is expected that the future environmental risk of pesticides will be influenced by two key variables: climate change, which will affect pesticide exposure patterns, and pesticide management, which can result in an increase or decrease of pesticide dosages given the prevalence of agricultural pests or the implementation of environmental protection policies such as the ´Farm-to-Fork` strategy. The consequences of these two key variables for aquatic ecosystems have been scarcely investigated and need to be addressed making use of prospective risk assessment models and realistic environmental scenarios.

During the last two decades, there has been notable progress in the use of mathematical models to quantify pesticide exposure concentrations and ecological risks, including probabilistic methods (EUFRAM, 2006; Rico et al., 2021; Maertens et al., 2022). Among the available probabilistic risk assessment methods, Bayesian network models have arisen as innovative and flexible tools to explore the influence of different agricultural management scenarios on pesticide risks (Mentzel et al., 2022a), as well as for environmental assessments more generally (Kaikkonen et al., 2021). Differently to traditional regulatory approaches, probabilistic methods enable better consideration of uncertainty, and can incorporate spatial and temporal variability into pesticide exposure distributions, as well as distributions that represent the sensitivity of non-target species potentially affected by pesticides (Mentzel et al., 2022b; Piffady et al., 2021). Despite their potential to advance ecological risk assessments, examples of their application to characterize the influence of climate change or the implementation of new policies on chemical risk assessment is still limited (but see, Kaikkonen et al., 2021; Moe et al., 2021).

This study aimed to investigate how changes in future climate and pesticide use practices can affect the ecological risks of pesticides in a protected Mediterranean coastal wetland impacted by intensive rice farming. Our study serves as a basis to understand how future temperature and precipitation patterns, and the implementation of the Farm-to-Fork strategy, can affect aquatic pesticide exposure in rice paddies and ecological risks. The assessment shown here is grounded on probabilistic risk assessment and allows calculation of acute and chronic risk distributions for aquatic ecosystems using a Bayesian network approach. This work is one of the first assessing the risks of pesticide pollution from rice cultivation areas in the Mediterranean region at large spatial and temporal scales, and provides recommendations as to which pesticides should be targeted in future monitoring campaigns.

2. Materials and methods

2.1. Study area

The Albufera Natural Park (ANP) is located in eastern Spain (Fig. 1) and is one of the most studied Mediterranean coastal wetlands (Martínez-Megías and Rico, 2022). It is formed by a coastal lagoon surrounded by intensive rice production and a marsh area (Soria, 2006). The ANP joined the Natura 2000 as Site of Community Importance (SCI) in 1989 and is considered a Special Birds Protection Area (SBPA), being one of the most important Ramsar wetlands of Spain. Despite its regulation status, pesticides are heavily used during the rice cultivation period in the rice fields located inside the natural park. Several types of herbicides are used to control gramineous weeds (e.g. *Echinocloa* sp., *Leptochloa* sp.), Cyperaceae (*Chara* sp.) and wild rice; insecticides are applied to combat different aphid species; and fungicides are used to prevent rice blast fungus (*Magnaporthe grisea*). The rice paddies are hydrologically connected with the surrounding ditches and constitute the habitat and food source for many aquatic organisms, including several endangered species. Therefore, the impact of these pesticides on the diversity and abundance of aquatic organisms within the rice cultivation area is expected to have serious consequences for the aquatic diversity of the whole ANP.

In the ANP, rice is planted between May and September, with narrow time variations depending on farmers´ management. Seeding is done with dried fields. Plant germination takes place one week after seeding. The water depth in the rice fields is maintained through constant irrigation at approximately 10 cm during the whole growing season, except for four emptying events, which are required for the application of the pesticides. The first three emptying events correspond with herbicide applications that take place between 1 and 6 weeks since rice seeding and have a duration of approximately three days. During early July (8 weeks since seeding), the water fields are emptied for approximately 7 days. The purpose of this last drainage process (locally called *eixugó*) is to prevent the proliferation of some competing plant species such as *Echinocloa* sp., as well as the application of herbicides and insecticides. Fungicides are applied in late summer by helicopter without water removal. Harvesting takes place around the last week of September, after the paddy fields have been completely dried. The rice cultivation phases and pesticide applications are summarized in Fig. 2.

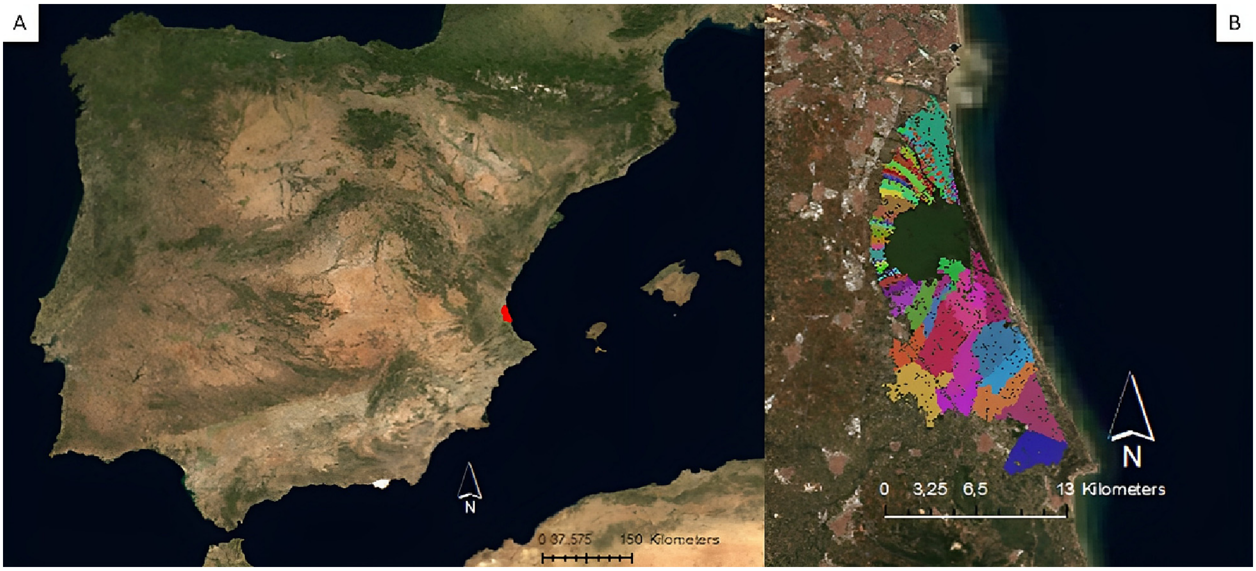

Fig. 1. A: location of ANP in the Iberian Peninsula (red area). B: View of the Albufera coastal lake and their surrounding rice plots forming the ANP. Colored polygons indicate hydrological clusters (i.e., rice plots with similar water renewal rate and water balance) used in the pesticide exposure modelling.

2.2. Study design and scenarios

Pesticide risks were assessed for the nine pesticides applied during the rice growing season (Fig. 2) using nine scenarios that describe differences between baseline and future climate conditions and pesticide application (Table 1). Weather data representing each climatological scenario were obtained for the rice growing season (May–October) and consisted of mean daily temperature (°C), daily total precipitation (cm) and daily evapotranspiration (cm). Meteorological data for the year 2008 was obtained from ©AEMET (2021) and was used to build the baseline climate scenario, while 2050 and 2100 forecasts were used to predict pesticide exposure in paddies in the mid- and long-term, respectively, after carefully evaluating that the weather data for these years was representative for the surrounding years. Weather projections were obtained from the Max Planck Institute Earth System Model at base resolution (MPI-ESM-LR, Giorgetta et al., 2013), as it is one of the few available models proposed by ©AEMET (2021) which has calculated weather forecasts for the closest meteorological station (Valencia, Spain). This model has been considered appropriate in other studies performed in the Júcar River Basin (Pool et al., 2021) and in other regions of Spain (Fernández et al., 2017). The model predictions are based on the Representative Concentration Pathway (RCP) 8.5 emission scenario, which represents the worst-case scenario for CO_2 emissions through the 21st century without considering any mitigation measures (Pool et al., 2021). The rest of emission scenarios were not included as they did not have precipitation data available.

Pesticide dosages recommended by the manufacturers were used to simulate the baseline (2008) scenario and the 2050 and 2100 scenarios, while additional scenarios with increased pesticide and reduced pesticide dose were defined considering 50 % more and less the recommended dose. The increased dosage is based on pesticide use trends indicated by local farmers, which claimed low pesticide efficacy to increasing pest prevalence and resistance, and the need to increase dosages to minimize the use of manpower for the elimination of unwanted weeds. The reduced dosage is based on the environmental target set by the European ́Farm-to-Fork` strategy to reduce agricultural dependance on pesticides and lower environmental risks (European Commission, 2021).

2.3. Pesticide exposure assessment

In this study, the rice production area of the ANP (210 km^2) was divided into hydrological rice-production clusters. This was achieved by retrieving cadastral cartographic data from the government of Spain and filtering it to

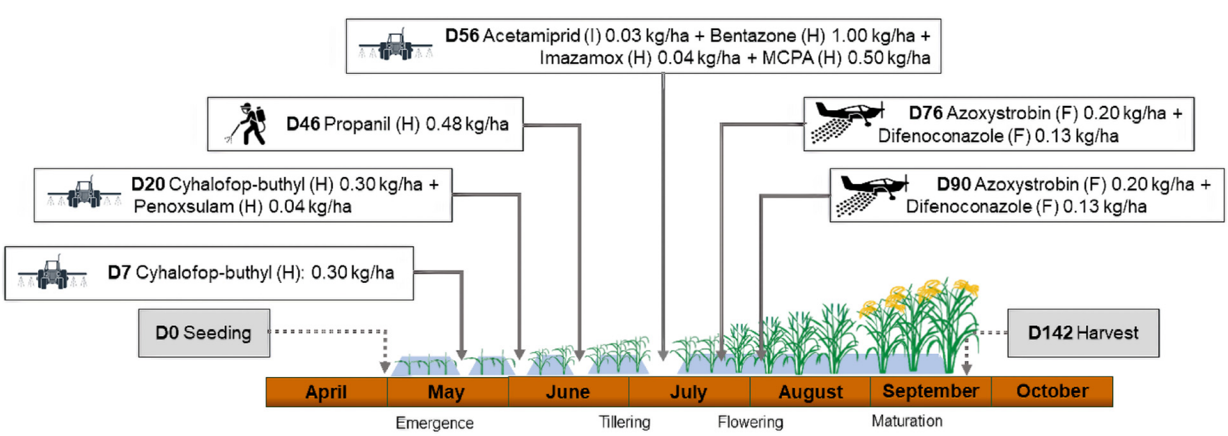

Fig. 2. Rice cultivation phases and pesticide applications in the rice fields of the Albufera Natural Park, including mode of application (i.e., truck, back-pack, helicopter) and dosage. D: day relative to seeding; F: fungicide; H: herbicide; I: insecticide.

Table 1
Climate and pesticide use scenarios used in this study.

Scenario name	Abbreviation	Input data	
		Meteorological data	Pesticide dose
Baseline	2008	2008	recommended
Mid-term projection	2050	2050	recommended
Long-term projection	2100	2100	recommended
Baseline, increasing pesticide dose	2008+	2008	50 % higher
Mid-term projection, increasing pesticide dose	2050+	2050	50 % higher
Long-term projection, increasing pesticide dose	2100+	2100	50 % higher
Baseline, reduced pesticide dose	2008-	2008	50 % lower
Mid-term projection, reduced pesticide dose	2050-	2050	50 % lower
Long-term projection, reduced pesticide dose	2100-	2100	50 % lower

select only areas designated for rice cultivation. Based on cartographical data for the irrigation ditches of the Natural Park, polygons were created, and the ditches were segmented longitudinally every 500 m in accordance with those polygons. Then, the centroid of the ditch segment was calculated. The rice paddies were clustered based on the Euclidean distance to the nearest centroid of the segmented ditch, resulting in 552 rice-production clusters. The steps followed to carry out this process are shown in the Supplementary Material (Fig. S1).

The data on the water irrigation rate of each rice production cluster was defined using a monitoring study of flow rates in 62 irrigation channels within the Natural Park in 2008 (Fig. S2). Additionally, we set 8 points on the southern part of the Natural Park due to the paucity of measures in that area with the mean values of the sample. Renewal rates were assigned to the clusters based on its flow rate and total surface. The complete calculation of water renewal rates is shown in the Supplementary Material (Text S1).

The start date of the rice cultivation in each cluster was assigned following a stochastic approach. Ten cases were defined based on the starting day of the rice growing season (from May 3rd to May 12st), maintaining constant the crop shift shown in Fig. 2. Then, based on the no spatial correlation with rice planting starting dates, nor crop durations in the study area, those cases were assigned randomly to each of the 552 rice production clusters.

Pesticide exposure concentrations in each cluster were predicted using the RICEWQ model, version 1.92 (Waterborne Environmental Inc). Its core equations involve pesticide processes occurring in the air compartment (i.e., drift, volatilization, wash-off, crop interception), the aquatic compartment (i.e., biological and chemical decay, drainage, transformation, sorption) and the interphase between water and sediment (i.e., settling, resuspension, seepage, diffusion). The RICEWQ model runs were based on the study region's specific rice-paddies, meteorological and hydrological parameters. The rice paddy parameters were obtained from field measurements and included some default RICEWQ model parameters (Tables S1 and S3). The meteorological data used for the RICEWQ simulations was the one described above for the selected scenarios. Since the selected prediction model did not have data for daily mean temperature, this parameter was estimated from the arithmetic mean of the daily maximum and minimum temperature. Furthermore, the daily mean temperature data obtained were used to calculate the evapotranspiration data. Details of evapotranspiration calculations are provided in the Supplementary Material (Text S2). Water irrigation and drainage were set by the renewal rate assigned to each of the clusters, the gains (rainfall) and losses (evapotranspiration) of the selected scenarios to keep a water depth of 10 cm during the rice growing season. The water balance also considered the four drainage events (D7, D20, D46, D56) for pesticide application described in Fig. 2. The equations used to derive the water balance are provided in the Supplementary Material (Text S3). Physico-chemical data for the nine pesticides evaluated in this study were mainly retrieved from the Draft Assessment Reports (DAR) published by the European Food Safety Authority (EFSA) and the Pesticide Properties Database (PPDB). These are shown in the Supplementary Material (Table S2).

Pesticide exposure concentrations in the paddy field water for each of the 9 pesticides were assessed for the 552 clusters in each of the 9 scenarios described in Table 1, yielding a total of 44,712 model runs. To perform all these model runs, a handler for the RICEWQ, named autoRICEWQ, was developed. This software automatically creates the input files, executes RICEWQ and process the output data for each run. All the details for the autoRICEWQ generated for this study can be found at Fuentes-Edfuf and Martínez-Megías (2022) (open source under GPL-3.0 License, programmed in Python 3). From the predicted pesticide exposure concentrations in the paddy field, we calculated the Peak Exposure Concentration (PEC) and the Time Weighted Average Concentration over a period of 21 days (TWAC21). Finally, a model distribution was fitted to the PEC and TWAC21 data obtained for the rice clusters in each scenario. The model distribution fitting was performed with the *fitdistrplus* R package (Delignette-Muller and Dutang, 2015) and the best fitting distribution was selected using the Akaike Information Criterion.

2.4. Pesticide effect assessment

Laboratory toxicity data for primary producers, invertebrates, and vertebrates for the studied pesticides were obtained from the ECOTOXicology Knowledgebase, U.S. Environmental Protection Agency. http:/www.epa.gov/ecotox/ (data downloaded on the 8th of February of 2022). The available data were screened and classified according to the criteria described by Rico et al. (2019). Briefly, acute toxicity data for vertebrates were based on 2–4 days LC50 values, for invertebrates on 2–4 days LC50 or EC50 (immobilization), and for primary producers on EC50 (growth rate inhibition or yield) using an exposure period of 3–5 days for algae and >7 days for macrophytes. Chronic toxicity data for vertebrates were based on EC10 or NOECs (growth rate, development, behavior, mortality, immobilization) for an exposure period higher than 21 d, for invertebrates on EC10 or NOECs using similar endpoints and exposure durations as for vertebrates, and for primary producers based on EC10 or NOEC values for the same exposure duration and endpoints as for the acute assessment.

Acute and chronic Species Sensitivity Distributions (SSDs) were built using the available toxicity data by fitting a log-normal distribution with the MOSAIC software (King et al., 2013). In most cases, there were toxicity values for 8 or more taxa to build the acute or chronic SSDs; however, when there was toxicity data for <8 taxa, acute-to-chronic extrapolations were applied. In this way, acute SSDs were complemented with chronic EC10 or NOECs for unrepresented taxa by multiplying them by a factor of 100 for invertebrates and vertebrates, and 10 for primary producers. Chronic SSDs were complemented with acute EC50 or LC50 values by dividing them by a factor of 100 for invertebrates and vertebrates, and 10 for primary producers. The mean and standard deviation of the calculated SSDs for each pesticide are shown in Table S4.

2.5. Probabilistic risk assessment

Bayesian networks are probabilistic graphical models composed of nodes (variables) connected through arcs (displayed as arrows pointing from parent nodes to child nodes). Nodes are composed of discrete and mutually exclusive states (e.g. concentration intervals), to which prior probabilities are assigned (Bromley, 2005). The arcs represent conditional probability tables, which define the probability distribution of a child node for all possible combination of the states of the parent nodes (Aguilera et al., 2011; Kaikkonen et al., 2021). This direct acyclic graph uses the Bayes' rule to update the probability distributions of the network nodes and to calculate the risk distribution (Carriger et al., 2016; Kanes et al., 2017). The resulting distribution of the child node is also referred to as posterior probability (Pollino and Henderson, 2010; Molina et al., 2010). BN models can function as metamodels, integrating information and knowledge from several sources (e.g. literature) and sub-models (e.g. process-based prediction models such as RICEWQ) into a single predictive tool.

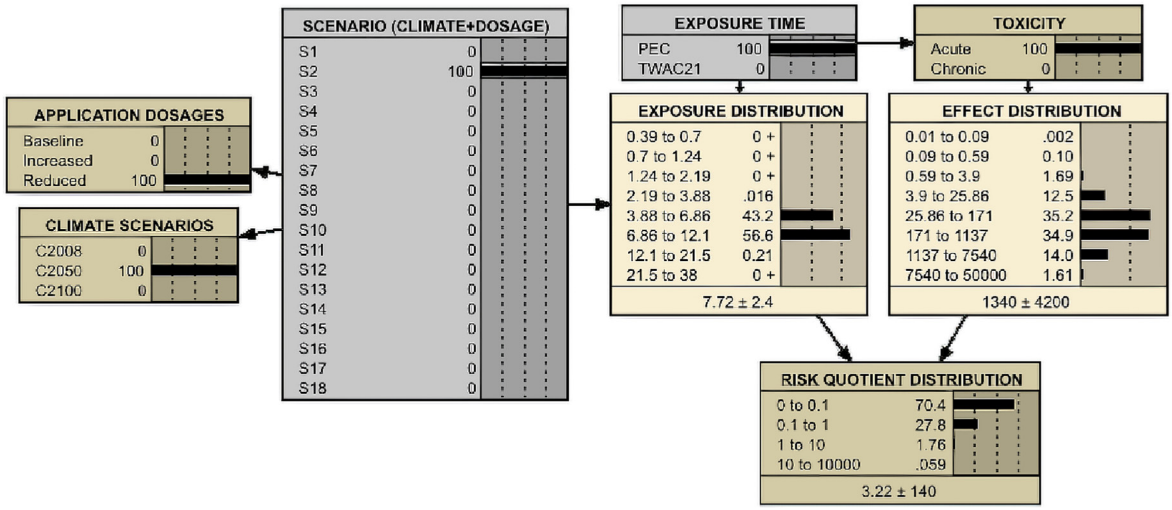

Fig. 3. Example of a Bayesian Network for the fungicide difenoconazole obtained with the Netica software. The boxes indicate the nodes and the arrows the arcs. The overview of the BN nodes is shown in Table S5.

In this study, a Bayesian network model was used for two main purposes: (1) to facilitate a probabilistic risk characterisation by calculating a probability distribution (posterior probability) of Risk Quotients (RQ) based on the exposure and effect distribution using the Bayes´ Theorem (Bolstad and Curran, 2016), and (2) to integrate different climate and pesticide management scenarios into one single framework. The Bayesian networks were built with the Netica software (Norsys Software Corp., www.norsys.com) using the guidelines provided by Marcot et al. (2006) and Pollino and Henderson (2010). The Bayesian network approach used in this study followed a simplified structure of the one carried out by Mentzel et al. (2022a), and was composed of 8 nodes (Fig. 3).

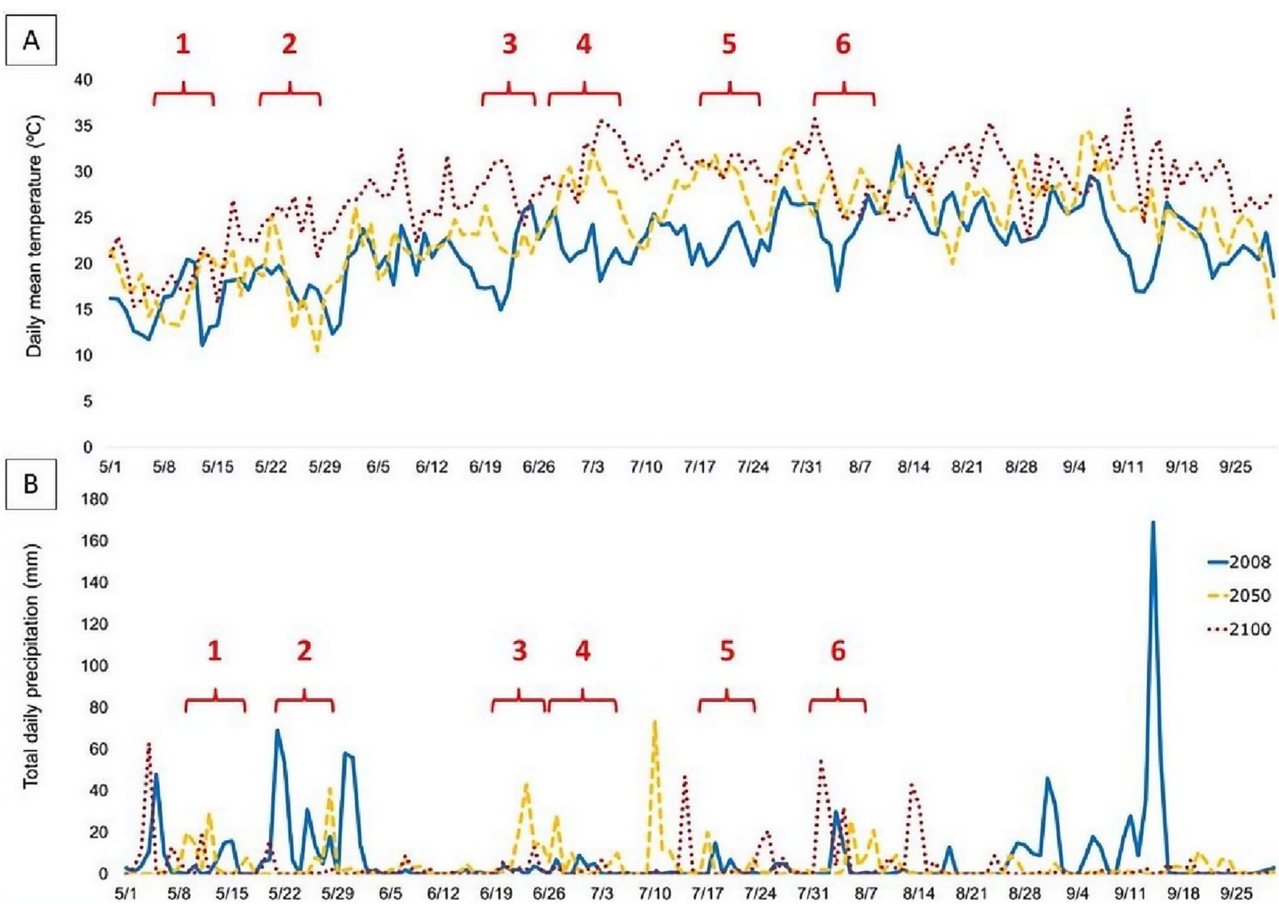

Fig. 4. Variation of mean daily temperature (A) and total daily precipitation (B) over the rice cultivation period. Each line represents a different climate scenario (i.e., 2008, 2050, 2100) predicted by the MPI-ESM-LR model. The red numbers indicate pesticide application events: 1: cyhalofop (1st) (D7); 2: cyhalofop (2nd) and penoxsulam (D20); 3: propanil (D46); 4: acetamiprid, bentazon, imazamox and MCPA (D56); 5: azoxystrobin and difenoconazole (1st); 6: azoxystrobin and difenoconazole (2nd). See Fig. 1 for a detailed description of the pesticide dosages and modes of application.

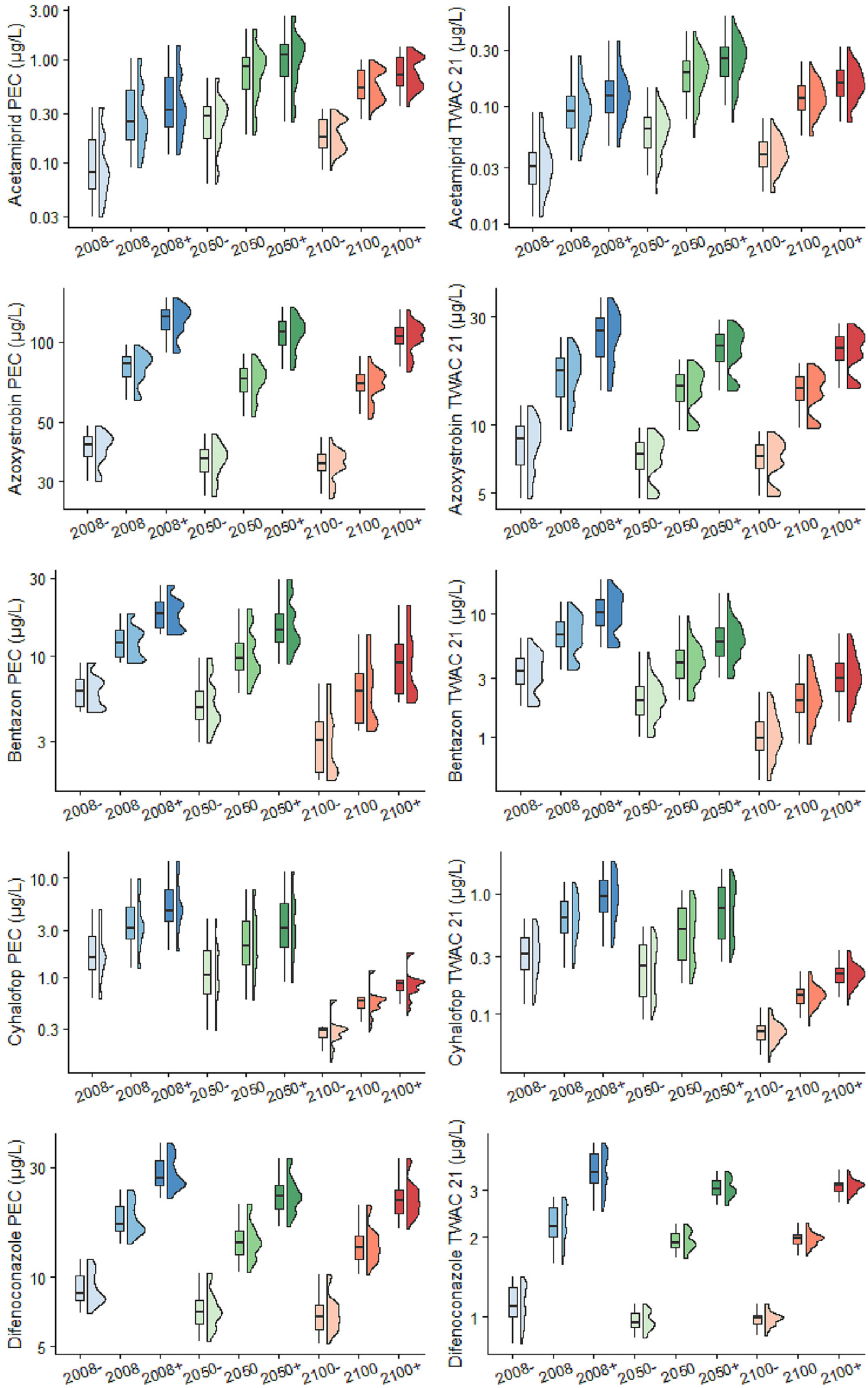

Fig. 5. Peak Exposure Concentration (PEC) and highest Time Weighted Average Concentration (TWAC) distributions for the nine pesticides evaluated in this study within each scenario. The box plot shows the median of the distribution (bold line) as well as the 25th and 75th percentiles. See Table 1 for a description of the pesticide scenario abbreviations.

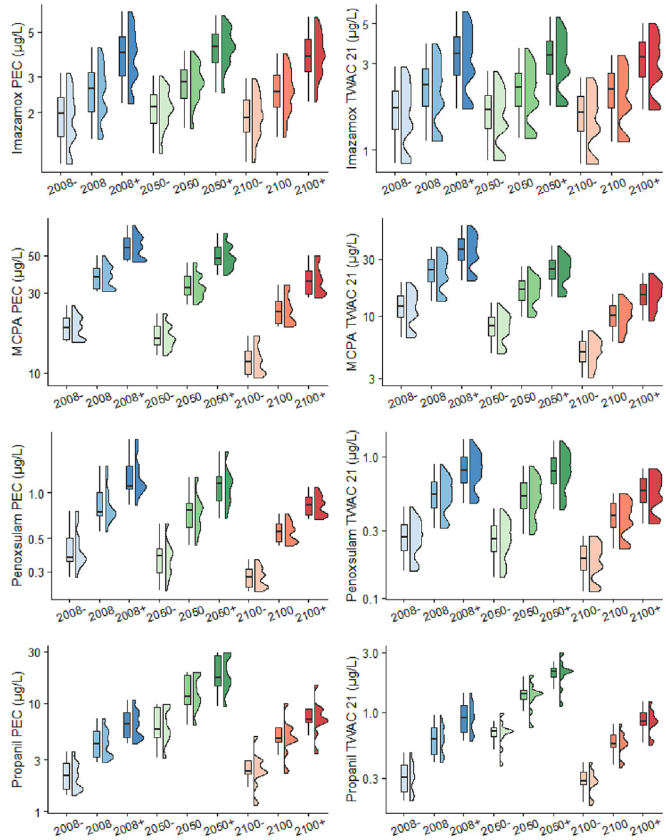

Fig. 5 (*continued*).

The exposure concentration distribution node was determined by the scenario combination and the exposure time (acute or chronic). This node used the exposure distributions fitted to the RICEWQ model exposure concentrations described above. The ranges of the exposure concentration distribution included in the Netica software were determined separately for each pesticide. Briefly, the lower limit of the exposure distribution for a given pesticide was set as the minimum TWAC21 value divided by two, and the upper limit was set as the maximum PEC. Then, the bin sizes were automatically derived by the Netica software by dividing this data interval into 8 bins using a multiplicative factor (see Fig. 3).

The effect concentration distribution node was based on the fitted acute and chronic SSDs described above. For this node, the lower limit was set as the minimum toxicity value for the selected pesticide divided by 10, and the upper limit as the highest toxicity value multiplied by 10. The same approach as described above for the exposure distribution was used for the calculation of the bin sizes.

The Risk Quotient (RQ) distribution for each pesticide was calculated as the ratio between values within the exposure and the effect distributions, considering the PEC/acute SSD and the TWAC21/chronic SSD for the acute and chronic risk assessments, respectively. As shown in Fig. 3, RQs were classified into 4 categories (i.e., based on 4 established bins). RQs below 0.1 were considered to result in no risks for aquatic ecosystems; RQs larger than 0.1 and lower than 1 were considered to result in potential risks; RQs between 1 and 10 were assumed to represent moderate risks, and RQs larger than 10 were considered to pose high risks.

3. Results and discussion

3.1. Pesticide exposure assessment

The three climate scenarios were significantly different, both in terms of daily mean temperature and total precipitation for the whole crop season (Fig. 4). The mean daily temperature (±SD) was 20.9 ± 4.1 °C for 2008, 23.7 ± 4.8 °C for 2050 and 27.4 ± 4.4 °C for 2100. Regarding annual precipitation, it amounted to 1759 mm for 2008, 1301 mm for 2050, and 784 mm for 2100. The results of the exposure assessment show that the different weather projections for 2008, 2050 and 2100 notably affected pesticide exposure distributions (Fig. 5). For most pesticides, the increase in temperatures and the reduction in precipitation of the 2050 and 2100 scenarios resulted in a decrease of predicted exposure concentrations, which in general was more evident for the PEC distributions as compared to the TWAC ones. However, for other pesticides such as acetamiprid or imazamox, the exposure distributions in the different time horizons were rather comparable, while propanil showed higher PEC and TWAC distributions in 2050 as compared to 2008 and 2100 due to precipitation peaks during the time of pesticide application (see Fig. 5 and Fig. S3).

The observed trend towards a reduction of PEC and TWACs for most pesticides in the 2050 and 2100 scenarios could be related to processes such as volatilization (Bloomfield et al., 2006; Noyes et al., 2009) and microbial biodegradation in water or sediment (Delcour et al., 2015). These processes were enhanced by increasing temperatures as described in the equations that support the RICEWQ calculations. For compounds such as acetamiprid or imazamox, the slight differences in PEC or TWACs among the three environmental scenarios could be related to their application type and their specific physico-chemical properties. For example, imazamox is applied directly to dried soils and shows a very low degradation rate in soil, therefore temperature is expected to affect much less this process. Acetamiprid, is also applied directly to soil during the 7-day dry period (i.e., the *eixugó* period). For both pesticides, PECs were driven by soil resuspension after rewetting, a process that is related to agricultural irrigation practices. As for propanil, the higher water concentration predicted for the 2050 scenario is closely related to heavy precipitation events occurring during or shortly after the pesticide application date (around D46), which influenced pesticide wash-off from the rice plants and sediment resuspension. In line with this, some studies, such as Nolan et al. (2008) or Lewan et al. (2009) indicate the timing of precipitation events in relation to pesticide application dates and drainage losses as one of the main drivers of peak exposure concentrations in water bodies.

Regardless of the climatic projections, variations in pesticide application dosages resulted in marked PEC and TWAC distribution differences as compared to the recommended dosages (Fig. 5). Differences in exposure distributions resulting from the different dosage scenarios were particularly noticeable for PECs of the fungicides azoxystrobin and difenoconazole, which are applied in periods in which the paddy fields were filled with water, so that a fraction of the applied dosage is directly dissolved into the rice plot water. Notably, variations in pesticide contamination in paddy field water related to the different application scenarios tested in this study were more prominent than variations in pesticide exposure related to the 2050 and 2100 weather projections provided by the RCP 8.5 emission scenario. This suggests that, within this century, pesticide use management is likely more important than climate change factors to determine environmental exposure.

3.2. Ecological risk assessment

The Bayesian network predicted acute and chronic RQ distributions as the ratio between the exposure distributions and the SSDs (Fig. 6). For most pesticides, the percentage of cases with moderate or high acute risks in the baseline scenario was relatively low (<5 %). Exceptions were the fungicides azoxystrobin and difenoconazole, with a probability of 16 % of the cases showing a moderate risk. Regarding chronic risks, for the baseline scenarios, azoxystrobin, difenoconazole, MCPA, imazamox and penoxsulam had a probability of 5 % of the cases of being at a moderate to high risk level. The compounds posing the largest chronic risks were azoxystrobin, difenoconazole, and MCPA, with 54 %, 21 % and 13 % of the ANP rice clusters showing moderate or high chronic risks, respectively (Fig. 6).

The different climate projections (2050 and 2100) had a mild influence on the RQ distributions, despite the decrease in exposure concentrations described for some compounds in the previous section. The most noticeable

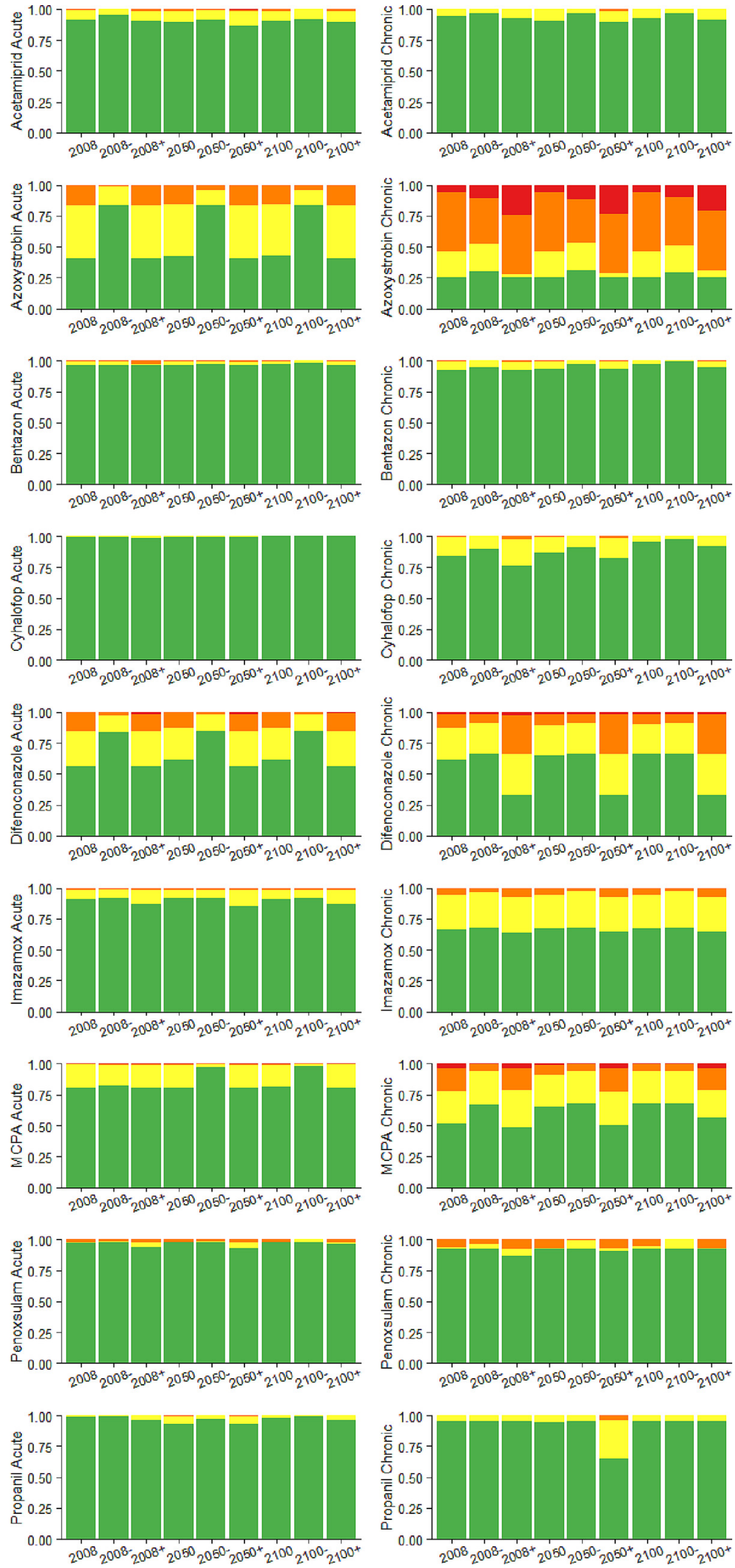

Fig. 6. Bar plots showing the fraction of acute and chronic Risk Quotients (RQs) for the different rice production clusters falling within each risk category. The colors indicate the risk categories: Green: no risk (RQs: 0–0.1); Yellow: potential risk (RQs: 0.1–1); Orange: moderate risk (RQs: 1–10); Red: high risk (RQs: 10–10,000). See Table 1 for a description of the pesticide scenario abbreviations.

influence was observed for the chronic RQ distribution of the herbicide MCPA, with a probability of rice clusters showing moderate or high risks decreasing from 21 % in the 2008 scenario, to 9 % in the 2050 scenario, and 6 % in the 2100 scenario. For propanil, the acute RQ distribution changed according to the PEC increase in 2050, indicating a larger probability of potential risks (7 % of cases) in that scenario as compared to the 2008 (1 %) and the 2100 (2 %) ones (Fig. 6).

The different pesticide dosage scenarios had a clear influence on the RQ distributions for the pesticides, particularly for those showing moderate and high risks in the 2008 scenario. For example, the percentage of rice production clusters showing moderate or high chronic risks for azoxystrobin in the scenario accounting for a reduction of 50 % of the dosage in the baseline scenario (i.e., 2008-) were 48 %, while the percentage in the scenario simulating a 50 % increase of the dose (i.e., 2008+) was 72 %. In line with the mild influence of the weather scenarios described above, the temporal changes in the RQ distribution of scenarios assuming a 50 % increase or decrease in the dosages was relatively low (Fig. 6).

3.3. Implications for risk assessment and way forward

This study shows how weather projections and environmental management strategies can be integrated into a probabilistic framework to characterize current and future risks of pesticides in a Mediterranean wetland of high ecological value. The approach allows integration of spatial-temporal variability in terms of hydrological regimes, weather conditions, and pesticide application schemes, and complements environmental monitoring studies that have shown unacceptable exposure levels for aquatic organisms in ditches and lagoons of the same study area (Calvo et al., 2021).

Our results show that the fungicides azoxystrobin and difenoconazole, and the herbicide MCPA, pose the largest ecotoxicological risks. Azoxystrobin and difenoconazole were introduced in the ANP as replacements of more toxic (prochloraz, tebuconazole), or recently banned (carbendazim) fungicides (Andreu Sánchez, 2008). However, as shown in this study, short and long-term ecological risks in the rice production area of the ANP may be expected. Semi-field experiments performed in Sweden and the Netherlands show chronic toxic effects of azoxystrobin at concentrations that are an order of magnitude lower than the TWACs calculated in this study, with copepods and some Cladocera showing the largest abundance declines (Gustafsson et al., 2010; van Wijngaarden et al., 2014). Difenoconazole has proven to be very toxic to daphnids (Moreira et al., 2020), fish and algae (Man et al., 2021) in other ecosystems impacted by rice production (Shen et al., 2022). On the other hand, MCPA is relatively toxic to eelgrass and dicotyledonous aquatic plants (Nielsen and Dahllöf, 2007), and has been highlighted as one of the most toxic compounds in other rice production areas such as the Ebro Delta in Spain (Barbieri et al., 2020).

Our study shows how climate conditions can influence pesticide exposure and risks. In this case-study, local precipitation events occurring around the time of pesticide applications were found to be more determinant than temperature increases forecasted for the next decades. Therefore, further attention should be paid to integrate changes in precipitation regimes, including extreme rainfall events, into future pesticide risk assessment scenarios for the Mediterranean region.

The outcomes of the risk assessment show that the implementation of environmental protection measures, such as the dose reduction measure promoted by the ´Farm-to-Fork` strategy, will be key to reduce the aquatic risks of pesticides in the next decades. However, the reduction in 50 % of the dose does not completely prevent risks for some pesticides. Additional risk reduction measures, such as the replacement of highly hazardous substances, the incorporation of integrated pest management practices or the construction of constructed wetlands can limit pesticide emissions to surrounding water bodies (Alexoaei et al., 2022; Martín et al., 2020; Pavlidis and Karasali, 2020; Silva et al., 2022). A recent study by Rodrigo et al. (2022) shows that two constructed wetlands located next to rice production areas can reduce metal loads and the number of pesticides entering the Albufera Lake. Further studies should be developed to calculate pesticide transport in the drainage ditches of the ANP and potential risks for aquatic communities in the Albufera Lake under different weather and pesticide management scenarios.

The modelling approach described here offers opportunities to predict pesticide risks in a complex spatial-temporal environmental setting; however, it has some caveats. On the one hand, it disregards the formation of hazardous pesticide metabolites and transformation products (Li, 2021). Accounting for the influence of temperature on pesticide transformation rates in the different scenarios and calculating risks for parent compounds and metabolites could have made the differences between the baseline and future risk scenarios less evident. Although the RICEWQ model includes some processes to account for metabolite formation, we found that the amount of data to characterize the influence of temperature on their formation rate and their ecotoxicological risks was too limited. Therefore, this aspect was not included as part of this study.

Another major limitation is that we characterized the sensitivity of aquatic ecosystems in the ANP using acute and chronic SSDs for a selection of (standard) test species, which are not necessarily representative for Mediterranean wetland ecosystems. Furthermore, the sensitivity of these aquatic ecosystems was considered to be constant over the 2050 and the 2100 climate scenarios (i.e., the same SSD parameters were used for the future scenario evaluations). Some studies suggest that aquatic organisms will have a higher sensitivity to pesticide exposure in scenarios of elevated (+5 °C) temperature (Camp and Buchwalter, 2016; Roth et al., 2022; Vilas-Boas et al., 2021). Therefore, our risk projections may have, to some extent, underestimated actual ecological risks. On the other hand, climate change, and the extreme weather events associated to it are expected to affect the structure of aquatic communities (Polazzo et al., 2022), filtering for species assemblages that may be more (or less) sensitive to different pesticides. These aspects should be further investigated and potentially incorporated into future pesticide risk projections for the Mediterranean region.

4. Conclusions

This study shows how Bayesian network approaches can be used to evaluate the influence of different climate change and pesticide management scenarios on the ecological risks of pesticides. The case-study performed here for the nine pesticides used in rice production in the ANP shows that future climate projections will result in lower exposure and risk distributions in scenarios dominated by an increase of temperatures, while exposure and risks can increase for some pesticides applied during periods of heavy precipitation events, which will be more recurrent in the future. Moreover, it shows that three out of the nine evaluated pesticides (azoxystrobin, difenoconazole and MCPA) pose high ecological risks for aquatic organisms and should be included in further ecotoxicological experiments and monitoring programs in the study area. Finally, we have demonstrated that the increase of pesticide dosages due to the higher prevalence of agricultural pests is going to increase the ecological risks for aquatic organisms in Mediterranean coastal wetlands, and that the implementation of pesticide use reduction programs, such as the European ´Farm-to-Fork` strategy, are crucial to reduce pesticide risks, although will need additional measures to completely prevent them.

CRediT authorship contribution statement

Claudia Martínez-Megías: Conceptualization, Formal analysis, Investigation, Methodology, Writing – original draft. **Sophie Mentzel:** Investigation, Software, Methodology, Writing – review & editing. **Yasser Fuentes-Edfuf:** Investigation, Software, Methodology, Writing – review & editing. **S. Jannicke Moe:** Investigation, Software, Methodology, Writing – review & editing. **Andreu Rico:** Conceptualization, Investigation, Methodology, Writing – original draft, Supervision, Funding acquisition.

Data availability

Data will be made available on request.

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.2023.163018.

References

Agencia Estatal de Meteorología (©AEMET), 2021. Servicios climáticos. Análisis estacional València. Consulted on 02 December 2021. www.aemet.es.
Aguilera, P.A., Fernández, A., Fernández, R., Rumí, R., Salmerón, A., 2011. Bayesian networks in environmental modelling. Environ. Model. Softw. 26 (12), 1376–1388. https://doi.org/10.1016/j.envsoft.2011.06.004.
Alexoaei, A.P., Robu, R.G., Cojanu, V., Miron, D., Holobiuc, A.M., 2022. Good practices in reforming the common agricultural policy to support the european green Deal – a perspective on the consumption of pesticides and fertilizers. Amfiteatru Economic 24 (60), 525–545. https://doi.org/10.24818/EA/2022/60/525.
Ali, E., Cramer, W., Carnicer, J., Georgopoulou, E., Hilmi, N., Le Cozannet, G., Lionello, P., 2022. CCP 4 Mediterranean region. Available atIn: Pörtner, H.-O., Roberts, D.C., Tignor, M., Poloczanska, E.S., Mintenbeck, K., Alegría, A., Craig, M., Langsdorf, S., Löschke, S., Möller, V., Okem, A., Rama, B. (Eds.), Climate Change 2022: Impacts, Adaptation and Vulnerability. Contribution of Working Group II to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press , pp. 2233–2272.. https://www.ipcc.ch/report/ar6/wg2/.
Andreu Sánchez, D.O., 2008. Evaluación de riesgos ambientales del uso de plaguicidas empleados en el cultivo del arroz en el parque natural de La albufera de Valencia. Universitat Politècnica de València.
Arenas-Sánchez, A., López-Heras, I., Nozal, L., Vighi, M., Rico, A., 2019. Effects of increased temperature, drought, and an insecticide on freshwater zooplankton communities. Environ. Toxicol. Chem. 38 (2), 396–411. https://doi.org/10.1002/etc.4304.
Barbieri, M.V., Peris, A., Postigo, C., Moya-Garcés, A., Monllor-Alcaraz, L.S., Rambla-Alegre, M., Eljarrat, E., López de Alda, M., 2020. Evaluation of the occurrence and fate of pesticides in a typical Mediterranean delta ecosystem (Ebro River Delta) and risk assessment for aquatic organisms. Environ. Pollut. 274. https://doi.org/10.1016/j.envpol.2020.115813.
Barhoumi, B., Clérandeau, C., Gourves, P.Y., Le Menach, K., Megdiche, Y.El, Peluhet, L., Budzinski, H., Baudrimont, M., Driss, M.R., Cachot, J., 2014. Pollution biomonitoring in the Bizerte lagoon (Tunisia), using combined chemical and biomarker analyses in grass goby, Zosterisessor ophiocephalus (Teleostei, Gobiidae). Mar. Environ. Res. 101 (1), 184–195. https://doi.org/10.1016/j.marenvres.2014.07.002.
Bloomfield, J.P., Williams, R.J., Gooddy, D.C., Cape, J.N., Guha, P., 2006. Impacts of climate change on the fate and behaviour of pesticides in surface and groundwater-a UK perspective. Sci. Total Environ. 369 (1–3), 163–177. https://doi.org/10.1016/j.scitotenv.2006.05.019.
Bolstad, W.M., Curran, J.M., 2016. Introduction to Bayesian Statistics. John Wiley & Sons.
Bromley, J., 2005. Guidelines for the Use of Bayesian Networks as a Participatory Tool for Water Resource Management. nerc.ac.uk.
Calvo, S., Romo, S., Soria, J., Picó, Y., 2021. 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. Sci. Total Environ. 774, 145009. https://doi.org/10.1016/j.scitotenv.2021.145009.
Camp, A.A., Buchwalter, D.B., 2016. Can't take the heat: temperature-enhanced toxicity in the mayfly Isonychia bicolor exposed to the neonicotinoid insecticide imidacloprid. Aquat. Toxicol. 178, 49–57. https://doi.org/10.1016/j.aquatox.2016.07.011.
Carriger, J.F., Martin, T.M., Barron, M.G., 2016. A Bayesian network model for predicting aquatic toxicity mode of action using two dimensional theoretical molecular descriptors. Aquat. Toxicol. 180, 11–24. https://doi.org/10.1016/j.aquatox.2016.09.006.
Ccanccapa, A., Masiá, A., Navarro-Ortega, A., Picó, Y., Barceló, D., 2016. Pesticides in the Ebro River basin: occurrence and risk assessment. Environ. Pollut. 211, 414–424. https://doi.org/10.1016/j.envpol.2015.12.059.
Delcour, I., Spanoghe, P., Uyttendaele, M., 2015. Literature review: impact of climate change on pesticide use. Food Res. Int. 68, 7–15.
Delignette-Muller, M.L., Dutang, C., 2015. Fitdistrplus: an R package for fitting distributions. J. Stat. Softw. 64 (4), 1–34. https://doi.org/10.18637/jss.v064.i04.
Duchet, C., Caquet, T., Franquet, E., Lagneau, C., Lagadic, L., 2010. Influence of environmental factors on the response of a natural population of Daphnia magna (Crustacea: Cladocera) to spinosad and Bacillus thuringiensis israelensis in Mediterranean coastal wetlands. Environ. Pollut. 158 (5), 1825–1833. https://doi.org/10.1016/j.envpol.2009.11.008.
Eitzinger, J., Trnka, M., Semerádová, D., Thaler, S., Svobodová, E., Hlavinka, P., Šiška, B., Takáč, J., Malatinská, L., Nováková, M., Dubrovský, M., Žalud, Z., 2013. Regional climate change impacts on agricultural crop production in central and Eastern Europe - hotspots, regional differences and common trends. J. Agric. Sci. 151 (6), 787–812. https://doi.org/10.1017/S0021859612000767.
EUFRAM, 2006. Concerted action to develop a European Framework for probabilistic risk assessment of the environmental impacts of pesticides September.
European Commission, 2021. The European Green Deal. . http://eurlex.europa.eu/resource.html?uri=cellar:208111e4-414e-4da5-94c1-852f1c74f351.0004.02/DOC_1&format=PDF.
Fernández, J., Casanueva, A., Montávez, J.P., Gaertner, M.Á., Casado, M.J., Manzanas, R., Gutiérrez, J.M., 2017. Regional climate projections over Spain: atmosphere. Future Climate projections. CLIVAR Exchanges. 73, pp. 39–44 September.
Fuentes-Edfuf, Y., Martínez-Megías, C., 2022. backmind/autoRICEWQ: v1.0.2. https://doi.org/10.5281/ZENODO.5940235.
Giorgetta, M.A., Jungclaus, J., Reick, C.H., Legutke, S., Bader, J., Böttinger, M., Brovkin, V., Crueger, T., Esch, M., Fieg, K., Glushak, K., Gayler, V., Haak, H., Hollweg, H.-D., Ilyina, T., Kinne, S., Kornblueh, L., Matei, D., Mauritsen, T., Stevens, B., 2013. Climate and carbon cycle changes from 1850 to 2100 in MPI-ESM simulations for the coupled model intercomparison project phase 5. J. Adv. Model. Earth Syst. 5 (3), 572–597. https://doi.org/10.1002/jame.20038.
Gustafsson, K., Blidberg, E., Elfgren, I.K., Hellström, A., Kylin, H., Gorokhova, E., 2010. Direct and indirect effects of the fungicide azoxystrobin in outdoor brackish water microcosms. Ecotoxicology 19 (2), 431–444. https://doi.org/10.1007/s10646-009-0428-9.
Hader, J.D., Lane, T., Boxall, A.B.A., Macleod, M., Di, A., 2022. Enabling forecasts of environmental exposure to chemicals in European agriculture under global change. Sci. Total Environ. 840 (March), 156478. https://doi.org/10.1016/j.scitotenv.2022.156478.
Holmstrup, M., Bindesbøl, A.M., Oostingh, G.J., Duschl, A., Scheil, V., Köhler, H.R., Loureiro, S., Soares, A.M.V.M., Ferreira, A.L.G., Kienle, C., Gerhardt, A., Laskowski, R., Kramarz, P.E., Bayley, M., Svendsen, C., Spurgeon, D.J., 2010. Interactions between effects of environmental chemicals and natural stressors: a review. Sci. Total Environ. 408 (18), 3746–3762. https://doi.org/10.1016/j.scitotenv.2009.10.067.
Kaikkonen, L., Parviainen, T., Rahikainen, M., Uusitalo, L., Lehikoinen, A., 2021. Bayesian networks in environmental risk assessment: a review. Integr. Environ. Assess. Manag. 17 (1), 62–78. https://doi.org/10.1002/ieam.4332.
Kanes, R., Ramirez Marengo, M.C., Abdel-Moati, H., Cranefield, J., Véchot, L., 2017. Developing a framework for dynamic risk assessment using Bayesian networks and reliability data. J. Loss Prev. Process Ind. 50, 142–153. https://doi.org/10.1016/j.jlp.2017.09.011.
King, G.K.K., Veber, P., Charles, S., Delignette-Muller, M.L., 2013. MOSAIC _ SSD : a new web-tool for the Species Sensitivity Distribution , allowing to include censored data by maximum likelihood. ArXiv, pp. 1–26 Preprint ArXiv:1311.5772.
Lamichhane, J.R., Dachbrodt-Saaydeh, S., Kudsk, P., Messéan, A., 2016. Toward a reduced reliance on conventional pesticides in European agriculture. Plant Dis. 100 (1), 10–24.. https://doi.org/10.1094/PDIS-05-15-0574-FE.
Lewan, E., Kreuger, J., Jarvis, N., 2009. Implications of precipitation patterns and antecedent soil water content for leaching of pesticides from arable land. Agric. Water Manag. 96 (11), 1633–1640. https://doi.org/10.1016/j.agwat.2009.06.006.
Li, Z., 2021. Improving screening model of pesticide risk assessment in surface soils: considering degradation metabolites. Ecotoxicol. Environ. Saf. 222, 112490. https://doi.org/10.1016/j.ecoenv.2021.112490.
Maertens, A., Golden, E., Luechtefeld, T.H., Hoffmann, S., Tsaioun, K., Hartung, T., 2022. Probabilistic risk assessment–the keystone for the future of toxicology. ALTEX 39 (1), 3.
Man, Y., Stenrød, M., Wu, C., Almvik, M., Holten, R., Clarke, J.L., Yuan, S., Wu, X., Xu, J., Dong, F., Zheng, Y., Liu, X., 2021. Degradation of difenoconazole in water and soil: kinetics, degradation pathways, transformation products identification and ecotoxicity assessment. J. Hazard. Mater. 418 (June). https://doi.org/10.1016/j.jhazmat.2021.126303.
Marcot, B.G., Steventon, J.D., Sutherland, G.D., Mccann, R.K., 2006. Guidelines for developing and updating Bayesian belief networks applied to ecological modeling and conservation. Can. J. For. Res. 36 (12), 3063–3074.
Martín, M., Hernández-Crespo, C., Andrés-Doménech, I., Benedito-Durá, V., 2020. Fifty years of eutrophication in the Albufera lake (Valencia, Spain): causes, evolution and remediation strategies. Ecol. Eng. 155 (April), 105932. https://doi.org/10.1016/j.ecoleng.2020.105932.
Martínez-Megías, C., Rico, A., 2022. Biodiversity impacts by multiple anthropogenic stressors in Mediterranean coastal wetlands. Sci. Total Environ. 818, 151712. https://doi.org/10.1016/j.scitotenv.2021.151712.
Mentzel, S., Grung, M., Holten, R., Tollefsen, K.E., Stenrød, M., Moe, S.J., 2022a. Probabilistic risk assessment of pesticides under future agricultural and climate scenarios using a Bayesian network. Frontiers in environmentalScience, 1645 https://doi.org/10.3389/fenvs.2022.957926.
Mentzel, S., Grung, M., Tollefsen, K.E., Stenrød, M., Petersen, K., Moe, S.J., 2022b. Development of a Bayesian network for probabilistic risk assessment of pesticides. Integr. Environ. Assess. Manag. 18 (4), 1072–1087. https://doi.org/10.1002/ieam.4533.
Moe, S.J., Carriger, J.F., Glendell, M., 2021. Increased use of Bayesian network models has improved environmental risk assessments. Integr. Environ. Assess. Manag. 17 (1), 53–61. https://doi.org/10.1002/ieam.4369.
Molina, J.L., Bromley, J., García-Aróstegui, J.L., Sullivan, C., Benavente, J., 2010. Integrated water resources management of overexploited hydrogeological systems using object-

oriented Bayesian networks. Environ. Model Softw. 25 (4), 383–397. https://doi.org/10.1016/j.envsoft.2009.10.007.
Moreira, R.A., de Araujo, G.S., Silva, A.R.R.G., Daam, M.A., Rocha, O., Soares, A.M.V.M., Loureiro, S., 2020. Effects of abamectin-based and difenoconazole-based formulations and their mixtures in Daphnia magna: a multiple endpoint approach. Ecotoxicology 29 (9), 1486–1499. https://doi.org/10.1007/s10646-020-02218-z.
Newton, A., Icely, J., Cristina, S., Brito, A., Cardoso, A.C., Colijn, F., Riva, S.D., Gertz, F., Hansen, J.W., Holmer, M., Ivanova, K., Leppäkoski, E., Canu, D.M., Mocenni, C., Mudge, S., Murray, N., Pejrup, M., Razinkovas, A., Reizopoulou, S., Zaldívar, J.M., 2014. An overview of ecological status, vulnerability and future perspectives of European large shallow, semi-enclosed coastal systems, lagoons and transitional waters. Estuar. Coast. Shelf Sci. 140, 95–122. https://doi.org/10.1016/j.ecss.2013.05.023.
Nielsen, L.W., Dahllöf, I., 2007. Direct and indirect effects of the herbicides glyphosate, bentazone and MCPA on eelgrass (Zostera marina). Aquat. Toxicol. 82 (1), 47–54. https://doi.org/10.1016/j.aquatox.2007.01.004.
Nolan, B.T., Dubus, I.G., Surdyk, N., Fowler, H.J., Burton, A., Hollis, J.M., Reichenberger, S., Jarvis, N., 2008. Identification of key climatic factors regulating the transport of pesticides in leaching and to tile drains. Pest Manag. Sci. 64, 933–944. https://doi.org/10.1002/ps.1587.
Noyes, P.D., McElwee, M.K., Miller, H.D., Clark, B.W., Van Tiem, L.A., Walcott, K.C., Erwin, K.N., Levin, E.D., 2009. The toxicology of climate change: environmental contaminants in a warming world. Environ. Int. 35 (6), 971–986. https://doi.org/10.1016/j.envint.2009.02.006.
Pavlidis, G., Karasali, H., 2020. Natural Remediation Techniques for Water Quality Protection and Restoration, pp. 327–340 https://doi.org/10.1007/978-3-030-48985-4_15.
Pérez-Ruzafa, A., Marcos, C., 2008. Coastal lagoons in the context of water Management in Spain and Europe. Sustainable Use and Development of Watersheds. 299–321. https://doi.org/10.1007/978-1-4020-8558-1_18.
Piffady, J., Carluer, N., Gouy, V., le Henaff, G., Tormos, T., Bougon, N., Adoir, E., Mellac, K., 2021. ARPEGES: a Bayesian belief network to assess the risk of pesticide contamination for the river network of France. Integr. Environ. Assess. Manag. 17 (1), 188–201. https://doi.org/10.1002/ieam.4343.
Pitacco, V., Mistri, M., Ferrari, C.R., Sfriso, A., Sfriso, A.A., Munari, C., 2020. Multiannual trend of micro-pollutants in sediments and benthic community response in a mediterranean lagoon (Sacca di goro, Italy). Water (Switzerland) 12 (4). https://doi.org/10.3390/W12041074.
Polazzo, F., Roth, S.K., Hermann, M., Mangold-Döring, A., Rico, A., Sobek, A., Van den Brink, P.J., Jackson, M.C., 2022. Combined effects of heatwaves and micropollutants on freshwater ecosystems: towards an integrated assessment of extreme events in multiple stressors research. Glob. Chang. Biol. 28 (4), 1248–1267. https://doi.org/10.1111/gcb.15971.
Pollino, C.A., Henderson, C., 2010. Bayesian networks : a guide for their application in natural resource management and policy. Landscape Logic, Technical Report. 14, p. 48.
Pool, S., Francés, F., Garcia-Prats, A., Pulido-Velazquez, M., Sanchis-Ibor, C., Schirmer, M., Yang, H., Jiménez-Martínez, J., 2021. From flood to drip irrigation under climate change: impacts on evapotranspiration and groundwater recharge in the Mediterranean region of Valencia (Spain). Earth's Future 9 (5), 1–20. https://doi.org/10.1029/2020EF001859.
Quintana, X.D., Boix, D., Gascón, S., Sala, J., 2018. Management and restoration of Mediterranean coastal lagoons in Europe (Càtedra d'). Gràfiques Agustí Printed.
Rico, A., Brock, T.C., Daam, M.A., 2019. Is the effect assessment approach for fungicides as laid down in the European food safety authority aquatic guidance document sufficiently protective for freshwater ecosystems? Environ. Toxicol. Chem. 38 (10), 2279–2293.
Rico, A., Dafouz, R., Vighi, M., Rodríguez-Gil, J.L., Daam, M.A., 2021. Use of postregistration monitoring data to evaluate the ecotoxicological risks of pesticides to surface waters: a case study with chlorpyrifos in the Iberian Peninsula. Environ. Toxicol. Chem. 40 (2), 500–512. https://doi.org/10.1002/etc.4927.
Rodrigo, M.A., Puche, E., Armenta, S., Juan, F., 2022. Two constructed wetlands within a Mediterranean natural park immersed in an agrolandscape reduce most heavy metal water concentrations and dampen the majority of pesticide presence. researchsquare.com.
Roth, S.K., Polazzo, F., García-Astillero Honrado, A., Cherta, L., Sobek, A., Rico, A., 2022. Multiple stressor effects of a heatwave and a herbicide on zooplankton communities: implications of global climate change. Frontiers in environmentalScience 2212.
Shen, C., Pan, X., Wu, X., Xu, J., Dong, F., Zheng, Y., 2022. Ecological risk assessment for difenoconazole in aquatic ecosystems using a web-based interspecies correlation estimation (ICE)-species sensitivity distribution (SSD) model. Chemosphere 289 (October 2021), 133236. https://doi.org/10.1016/j.chemosphere.2021.133236.
Silva, V., Yang, X., Fleskens, L., Ritsema, C.J., Geissen, V., 2022. Environmental and human health at risk – scenarios to achieve the farm to fork 50% pesticide reduction goals. Environ. Int. 165 (January), 107296. https://doi.org/10.1016/j.envint.2022.107296.
Soria, J.M., 2006. Past, present and future of La Albufera of Valencia Natural Park. Limnetica 25 (1–2), 135–142. https://doi.org/10.23818/limn.25.10.
van Wijngaarden, R.P.A., Belgers, D.J.M., Zafar, M.I., Matser, A.M., Boerwinkel, M.C., Arts, G.H.P., 2014. Chronic aquatic effect assessment for the fungicide azoxystrobin. Environ. Toxicol. Chem. 33 (12), 2775–2785. https://doi.org/10.1002/etc.2739.
Vilas-Boas, J.A., Arenas-Sánchez, A., Vighi, M., Romo, S., Van den Brink, P.J., Pedroso Dias, R.J., Rico, A., 2021. Multiple stressors in Mediterranean coastal wetland ecosystems: influence of salinity and an insecticide on zooplankton communities under different temperature conditions. Chemosphere 269. https://doi.org/10.1016/j.chemosphere.2020.129381.
Willming, M.M., Maul, J.D., 2016. Direct and indirect toxicity of the fungicide pyraclostrobin to Hyalella azteca and effects on leaf processing under realistic daily temperature regimes. Environ. Pollut. 211, 435–442. https://doi.org/10.1016/j.envpol.2015.11.029.

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Corrigendum

Corrigendum to "Influence of climate change and pesticide use practices on the ecological risks of pesticides in a protected Mediterranean wetland: A Bayesian network approach" [Sci. Total Environ. Volume 878 (2023), 163018]

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The authors express regret regarding the presence of errors in the printed version of the aforementioned article. The exposure assessment and risk assessment were based on forecasted precipitation values for the 2008, 2050 and 2100 scenarios that were not correct. The correct precipitation values for the 2008, 2050 and 2100 scenarios during the crop production season are 111, 64 and 57 mm, respectively. The version below shows the re-calculated exposure concentration distributions and the re-calculated risk distributions based on Bayesian networks, together with any modifications in the discussion. However, it should be noted that the corrections made here do not alter the overall conclusions of the study. The authors sincerely apologize for any inconvenience caused.

3. Results and discussion

Pesticide exposure assessment

The three climate scenarios were significantly different, both in terms of daily mean temperature and total precipitation for the whole crop season (Fig. 4). The mean daily temperature (±SD) was 22 ± 4 °C for 2008, 24 ± 5 °C for 2050 and 28 ± 4 °C for 2100. Regarding the precipitation values during crop season, they amounted to 111 mm for 2008, 64 mm for 2050, and 57 mm for 2100. The results of the exposure assessment show that the different weather projections for 2008, 2050 and 2100 notably affected pesticide exposure distributions (Fig. 5). For most pesticides, the increase in temperatures and the reduction in precipitation of the 2050 and 2100 scenarios resulted in a decrease of predicted exposure concentrations, which in general was more evident for the PEC distributions as compared to the TWAC ones. However, for other pesticides such as acetamiprid or imazamox, the exposure distributions in the different time horizons were rather comparable, while propanil showed higher PEC and TWAC distributions in 2050 as compared to 2008 and 2100 due to precipitation peaks during the time of pesticide application (see Figs. 5 and S3).

The observed trend towards a reduction of PEC and TWACs for most pesticides in the 2050 and 2100 scenarios could be related to processes such as volatilization (Bloomfield et al., 2006; Noyes et al., 2009) and microbial biodegradation in water or sediment (Delcour et al., 2015). These processes were enhanced by increasing temperatures as described in the equations that support the RICEWQ calculations. For compounds such as acetamiprid or imazamox, the slight differences in PEC or TWACs among the three environmental scenarios could be related to their application type and their specific physico-chemical properties. For example, imazamox is applied directly to dried soils and shows a very low degradation rate in soil, therefore temperature is expected to affect much less this process. Acetamiprid, is also applied directly to soil during the 7-day dry period (i.e., the *eixugó* period). For both pesticides, PECs were driven by soil resuspension after rewetting, a process that is related to agricultural irrigation practices. As for propanil, the higher

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water concentration predicted for the 2050 scenario is closely related to heavy precipitation events occurring during or shortly after the pesticide application date (around D46), which influenced pesticide wash-off from the rice plants and sediment resuspension. In line with this, some studies, such as Nolan et al. (2008) or Lewan et al. (2009) indicate the timing of precipitation events in relation to pesticide application dates and drainage losses as one of the main drivers of peak exposure concentrations in water bodies.

Regardless of the climatic projections, variations in pesticide application dosages resulted in marked PEC and TWAC distribution differences as compared to the recommended dosages (Fig. 5). Differences in exposure distributions resulting from the different dosage scenarios were particularly noticeable for PECs of the fungicides azoxystrobin and difenoconazole, which are applied in periods in which the paddy fields were flooded, so that a fraction of the applied dosage is directly dissolved into the rice plot water. Notably, variations in pesticide contamination in paddy field water related to the different application scenarios tested in this study were more prominent than variations in pesticide exposure related to the 2050 and 2100 weather projections provided by the RCP 8.5 emission scenario. This suggests that, within this century, pesticide use management is likely more important than climate change factors to determine environmental exposure.

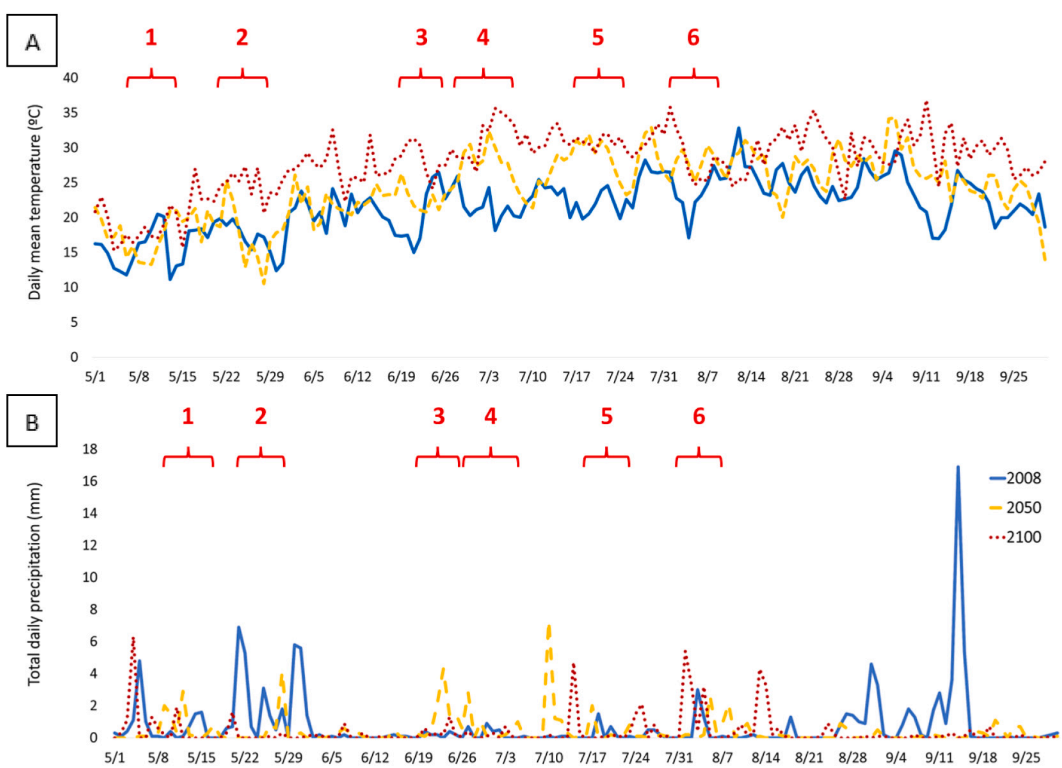
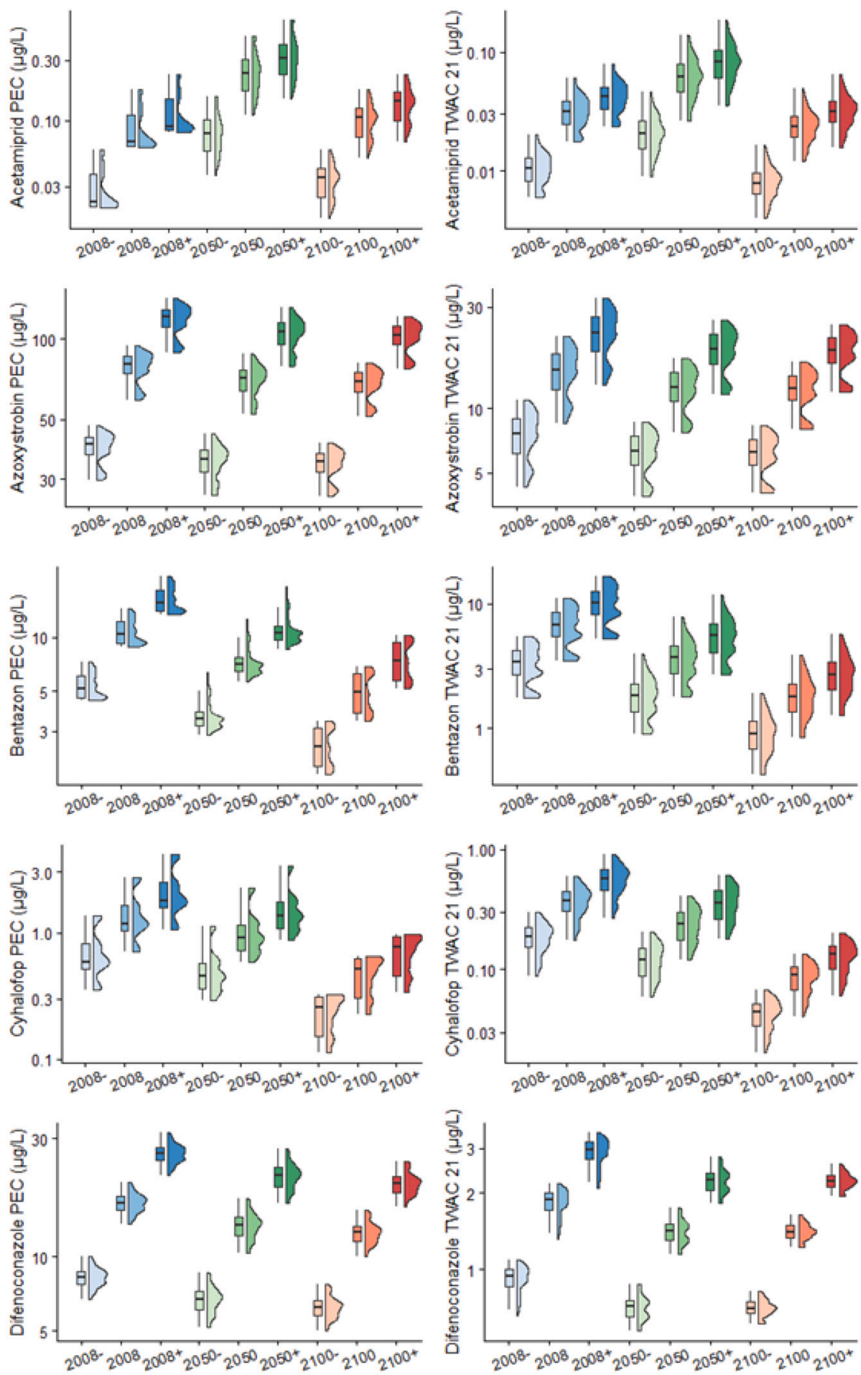


Fig. 4. (corrected). Variation of mean daily temperature (A) and total daily precipitation (B) over the rice cultivation period. Each line represents a different climate scenario (i.e., 2008, 2050, 2100) predicted by the MPI-ESM-LR model. The red numbers indicate pesticide application events: 1: cyhalofop (1st) (D7); 2: cyhalofop (2nd) and penoxsulam (D20); 3: propanil (D46); 4: acetamiprid, bentazon, imazamox and MCPA (D56); 5: azoxystrobin and difenoconazole (1st); 6: azoxystrobin and difenoconazole (2nd). See Fig. 1 for a detailed description of the pesticide dosages and modes of application.


Acetamiprid PEC (µg/L)
Acetamiprid TWAC 21 (µg/L)
Azoxystrobin PEC (µg/L)
Azoxystrobin TWAC 21 (µg/L)
Bentazon PEC (µg/L)
Bentazon TWAC 21 (µg/L)
Cyhalofop PEC (µg/L)
Cyhalofop TWAC 21 (µg/L)
Difenoconazole PEC (µg/L)
Difenoconazole TWAC 21 (µg/L)
2008- 2008 2008+ 2050- 2050 2050+ 2100- 2100 2100+

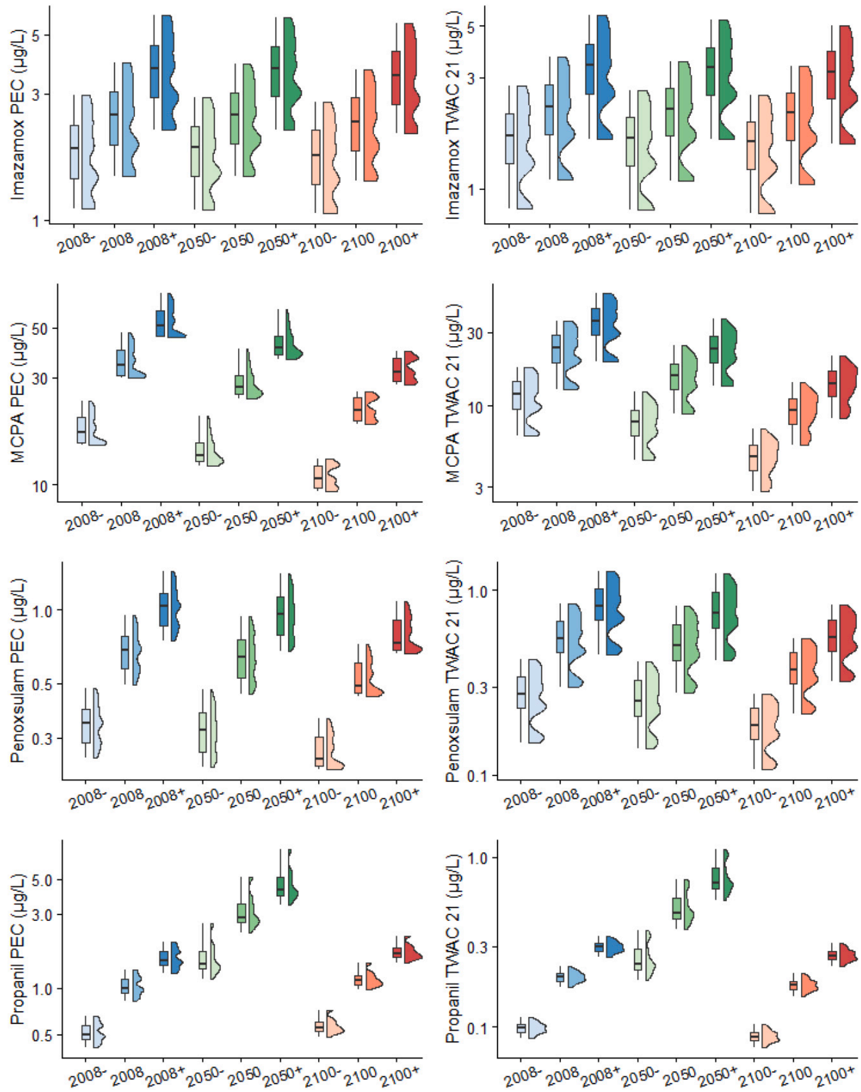


Fig. 5. (corrected). Peak exposure concentration (PEC) and highest time weighted average concentration (TWAC) distributions for the nine pesticides evaluated in this study within each scenario. The box plot shows the median of the distribution (bold line) as well as the 25th and 75th percentiles. See Table 1 for a description of the pesticide scenario abbreviations.

Ecological risk assessment

The Bayesian network approach predicted acute and chronic RQ distributions as the ratio between the exposure distributions and the SSDs (Fig. 6). For most pesticides, the percentage of rice clusters with moderate or high acute risks in the baseline scenario was relatively low (<5 %). Exceptions were the fungicides azoxystrobin and difenoconazole, with a probability of 28 % and 6 % of the rice clusters showing a moderate risk for the 2008 scenarios. Regarding chronic risks, for the baseline scenario, the following compounds showed significant moderate and high risks (>5 % of rice clusters): azoxystrobin (56 %), MCPA (12 %) and difenoconazole (6 %, Fig. 6).

The different climate projections (2050 and 2100) had a mild influence on the RQ distributions, despite the decrease in exposure concentrations described for some compounds in the previous section. One of the most striking influences was observed in the chronic distribution of MCPA, which shifted from a 12 % probability of moderate or high risk in rice clusters during the 2008 scenario to 8 % in the 2050 scenarios and 3 % in the 2100 scenario. Conversely, a contrasting trend was observed in the chronic distribution of azoxystrobin, with almost unnoticeable changes in the probability of rice clusters with moderate or high risks: 56 % in 2008, 52 % in 2050, and 55 % in the 2100 scenario (Fig. 6).

The different pesticide dosage scenarios had a clear influence on the RQ distributions for the pesticides, particularly for those showing moderate and high risks in the 2008 scenario. For example, the percentage of rice production clusters showing moderate or high chronic risks for azoxystrobin in the scenario accounting for a reduction of 50 % of the dosage in the baseline scenario (i.e., 2008-) were 30 %, while the percentage in the scenario simulating a 50 % increase of the dose (i.e., 2008+) doubled to 60 %. In line with the mild influence of the weather scenarios described above, the temporal changes in the RQ distribution of scenarios assuming a 50 % increase or decrease in the dosages was relatively low (Fig. 6).

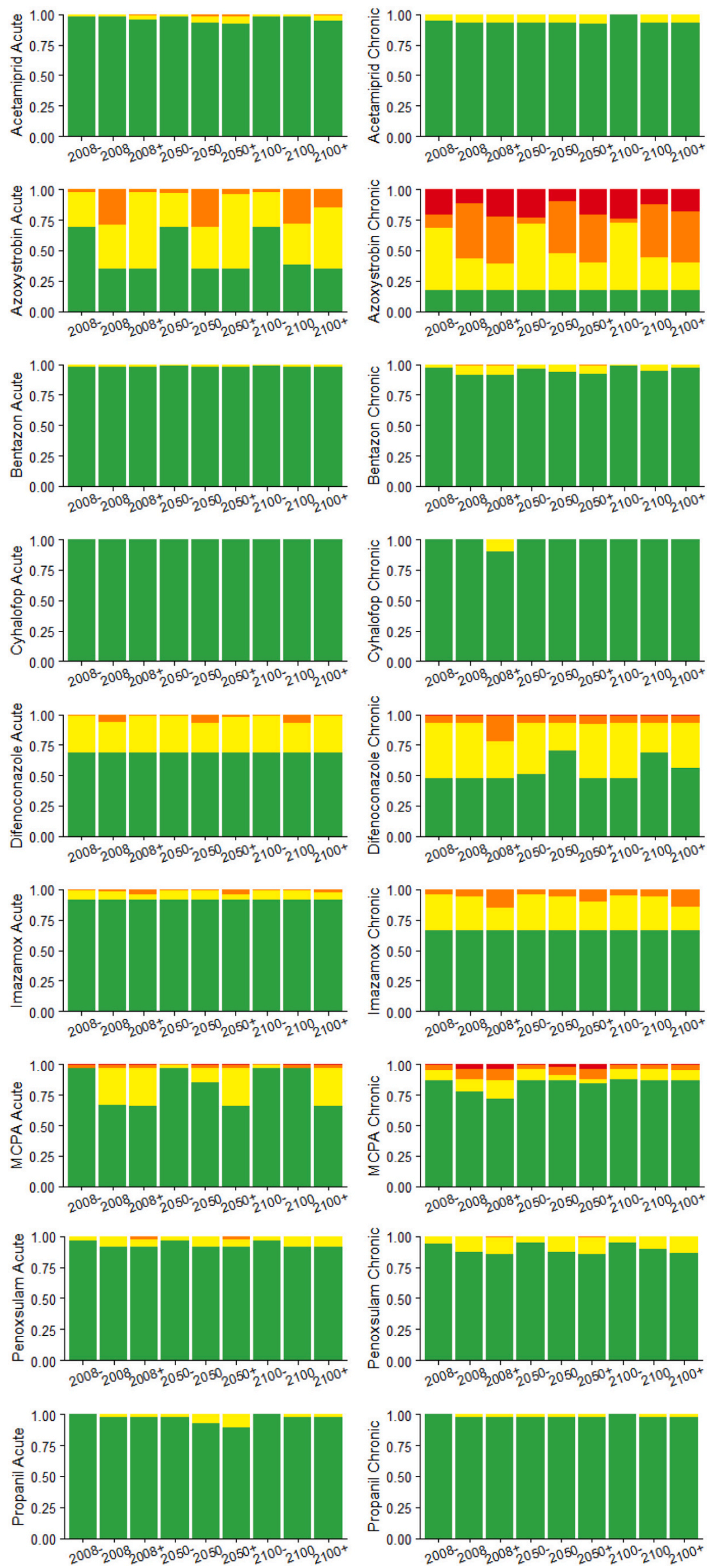


Fig. 6. Bar plots showing the fraction of acute and chronic risk quotients (RQs) for the different rice production clusters falling within each risk category. The colors indicate the risk categories: green: no risk (RQs: 0–0.1); yellow: potential risk (RQs: 0.1–1); orange: moderate risk (RQs: 1–10); red: high risk (RQs: 10–10,000). See Table 1 for a description of the pesticide scenario abbreviations.

Implications for risk assessment and way forward

This study shows how weather projections and environmental management strategies can be integrated into a probabilistic framework to characterize current and future risks of pesticides in a Mediterranean wetland of high ecological value. The approach allows integration of spatial-temporal variability in terms of hydrological regimes, weather conditions, and pesticide application schemes, and complements environmental monitoring studies that have shown unacceptable exposure levels for aquatic organisms in ditches and lagoons of the same study area (Calvo et al., 2021).

Our results show that the fungicides azoxystrobin and difenoconazole, and the herbicide MCPA, pose the largest ecotoxicological risks. Azoxystrobin and difenoconazole were introduced in the ANP as replacements of more toxic (prochloraz, tebuconazole), or recently banned (carbendazim) fungicides (Andreu Sánchez, 2008). However, as shown in this study, short and long-term ecological risks in the rice production area of the ANP may be expected. Semi-field experiments performed in Sweden and the Netherlands show chronic toxic effects of azoxystrobin at concentrations that are an order of magnitude lower than the TWACs calculated in this study, with copepods and some Cladocera showing the largest abundance declines (Gustafsson et al., 2010; van Wijngaarden et al., 2014). Difenoconazole has proven to be very toxic to daphnids (Moreira et al., 2020), fish and algae (Man et al., 2021) in other ecosystems impacted by rice production (Shen et al., 2022). On the other hand, MCPA is relatively toxic to eelgrass and dicotyledonous aquatic plants (Nielsen & Dahllöf, 2007), and has been highlighted as one of the most toxic compounds in other rice production areas such as the Ebro Delta in Spain (Barbieri et al., 2020).

Our study shows how climate conditions can influence pesticide exposure and risks. In this case-study, local precipitation events occurring around the time of pesticide applications were found to be more determinant than temperature increases forecasted for the next decades. Therefore, further attention should be paid to integrate changes in precipitation regimes, including extreme rainfall events, into future pesticide risk assessment scenarios for the Mediterranean region.

The outcomes of the risk assessment show that the implementation of environmental protection measures, such as the dose reduction measure promoted by the 'Farm-to-Fork' strategy, will be key to reduce the aquatic risks of pesticides in the next decades. However, the reduction in 50 % of the dose does not completely prevent risks for some pesticides. Additional risk reduction measures, such as the replacement of highly hazardous substances, the incorporation of integrated pest management practices or the construction of constructed wetlands can limit pesticide emissions to surrounding water bodies (Alexoaei et al., 2022; Martín et al., 2020; Pavlidis & Karasali, 2020; Silva et al., 2022). A recent study by Rodrigo et al. (2022) shows that two constructed wetlands located next to rice production areas can reduce metal loads and the number of pesticides entering the Albufera Lake. Further studies should be developed to calculate pesticide transport in the drainage ditches of the ANP and potential risks for aquatic communities in the Albufera Lake under different weather and pesticide management scenarios.

The modelling approach described here offers opportunities to predict pesticide risks in a complex spatial-temporal environmental setting; however, it has some caveats. On the one hand, it disregards the formation of hazardous pesticide metabolites and transformation products (Li, 2021). Accounting for the influence of temperature on pesticide transformation rates in the different scenarios and calculating risks for parent compounds and metabolites could have made the differences between the baseline and future risk scenarios less evident. Although the RICEWQ model includes some processes to account for metabolite formation, we found that the amount of data to characterize the influence of temperature on their formation rate and their ecotoxicological risks was too limited. Therefore, this aspect was not included as part of this study.

Another major limitation is that we characterized the sensitivity of aquatic ecosystems in the ANP using acute and chronic SSDs for a selection of (standard) test species, which are not necessarily representative for Mediterranean wetland ecosystems. Furthermore, the sensitivity of these aquatic ecosystems was considered to be constant over the 2050 and the 2100 climate scenarios (i.e., the same SSD parameters were used for the future scenario evaluations). Some studies suggest that aquatic organisms will have a higher sensitivity to pesticide exposure in scenarios of elevated (+5 °C) temperature (Camp & Buchwalter, 2016; Roth et al., 2022; Vilas-Boas et al., 2021). Therefore, our risk projections may have, to some extent, underestimated actual ecological risks. On the other hand, climate change, and the extreme weather events associated to it are expected to affect the structure of aquatic communities (Polazzo et al., 2022), filtering for species assemblages that may be more (or less) sensitive to different pesticides. These aspects should be further investigated and potentially incorporated into future pesticide risk projections for the Mediterranean region.

4. Conclusions

This study shows how Bayesian network approaches can be used to evaluate the influence of different climate change and pesticide management scenarios on the ecological risks of pesticides. The case-study performed here for the nine pesticides used in rice production in the ANP shows that future climate projections will result in lower exposure and risk distributions in scenarios dominated by an increase of temperatures, while exposure and risks can increase for some pesticides applied during periods of heavy precipitation events, which will be more recurrent in the future. Moreover, it shows that three out of the nine evaluated pesticides (azoxystrobin, difenoconazole and MCPA) pose high ecological risks for aquatic organisms and should be included in further ecotoxicological experiments and monitoring programs in the study area. Finally, we have demonstrated that the increase of pesticide dosages due to the higher prevalence of agricultural pests is going to increase the ecological risks for aquatic organisms in Mediterranean coastal wetlands, and that the implementation of pesticide use reduction programs, such as the European 'Farm-to-Fork' strategy, are crucial to reduce pesticide risks, although will need additional measures to completely prevent them.

Corrections to the Supplementary material

Influence of climate change and pesticide use practices on the ecological risks of pesticides in a protected Mediterranean wetland: A Bayesian network approach

Table S4
Pesticide exposure distribution parameters obtained with the RICEWQ model and species sensitivity distribution (SSD) parameters. Ac: acute toxicity; Chr: chronic toxicity; PEC: peak exposure concentrations; TWAC: time weighted average concentrations.

Compound	Scenarios	Exposure distribution		Effect distribution	
		Type	Parameters	Type	Parameters
Acetamiprid	PEC-2008-	Normal	Mean:0.03; sd: 0.01	Log-normal	Ac: 5.6 (meanlog), 3.6 (sdlog); Chr: 5.8 (meanlog), 4(sdlog)
	PEC-2008		Mean: 0.09; sd: 0.04		
	PEC-2008+		Mean: 0.12; sd: 0.05		
	PEC-2050-		Mean: 0.08; sd: 0.03		
	PEC-2050		Mean: 0.25; sd: 0.09		
	PEC-2050+		Mean: 0.33; sd: 0.12		
	PEC-2100-		Mean: 0.03; sd: 0.01		
	PEC-2100		Mean: 0.1; sd: 0.03		
	PEC-2100+		Mean: 0.14; sd: 0.04		
	TWAC-2008-		Mean: 0.01; sd: 0.003		
	TWAC-2008		Mean: 0.03; sd: 0.01		
	TWAC-2008+		Mean: 0.04; sd: 0.01		
	TWAC-2050-		Mean: 0.02; sd: 0.01		
	TWAC-2050		Mean: 0.06; sd: 0.02		
	TWAC-2050+		Mean: 0.09; sd: 0.03		
	TWAC-2100-		Mean: 0.01; sd: 0.003		
	TWAC-2100		Mean: 0.02; sd: 0.01		
	TWAC-2100+		Mean: 0.03; sd: 0.01		
Azoxystrobin	PEC-2008-	Normal	Mean: 39; sd: 4.9	Log-normal	Ac: 6.3 (meanlog); 1.5 (sdlog); Chr: 3.8 (meanlog); 3 (sdlog)
	PEC-2008		Mean: 78; sd: 9.9		
	PEC-2008+		Mean: 117; sd: 14		
	PEC-2050-		Mean: 35; sd: 4.7		
	PEC-2050		Mean: 70; sd: 9.4		
	PEC-2050+		Mean: 104; sd: 12		
	PEC-2100-		Mean: 33; sd: 4.3		
	PEC-2100		Mean: 67; sd: 8.6		
	PEC-2100+		Mean: 101; sd: 12.8		
	TWAC-2008-		Mean: 7.6; sd: 1.8		
	TWAC-2008		Mean: 15; sd: 3.7		
	TWAC-2008+		Mean: 22; sd: 5.6		
	TWAC-2050-		Mean: 6.2; sd: 1.4		
	TWAC-2050		Mean: 12; sd: 2.8		
	TWAC-2050+		Mean: 18; sd: 4.2		
	TWAC-2100-		Mean: 6.1; sd: 1.3		
	TWAC-2100		Mean: 12; sd: 2.6		
	TWAC-2100+		Mean: 18; sd: 3.9		
Bentazon	PEC-2008-	Normal	Mean: 5.3; sd: 0.84	Log-normal	Ac: 9.1 (meanlog); 2.7 (sdlog); Chr: 7 (meanlog); 2.1 (sdlog)
	PEC-2008		Mean: 10; sd: 1.68		
	PEC-2008+		Mean: 16; sd: 2.5		
	PEC-2050-		Mean: 3.7; sd: 0.73		
	PEC-2050		Mean: 7.3; sd: 1.46		
	PEC-2050+		Mean: 11; sd: 2.1		
	PEC-2100-		Mean: 2.5; sd: 0.52		
	PEC-2100		Mean: 5; sd: 1.2		
	PEC-2100+		Mean: 11; sd: 2.1		
	TWAC-2008-		Mean: 3.3; sd: 1.1		
	TWAC-2008		Mean: 6.7; sd: 2.2		
	TWAC-2008+		Mean: 10; sd: 3.4		
	TWAC-2050-		Mean: 1.8; sd: 0.68		
	TWAC-2050		Mean: 3.6; sd: 1.3		
	TWAC-2050+		Mean: 5.5; sd: 2		
	TWAC-2100-		Mean: 0.95; sd: 0.35		
	TWAC-2100		Mean: 1.9; sd: 0.71		
	TWAC-2100+		Mean: 2.85; sd: 1		
Cyhalofop-buthyl	PEC-2008-	Normal	Mean: 0.71; sd: 0.32	Log-normal	Ac: 7.6 (meanlog); 1.6 (sdlog); Chr: 4.1 (meanlog); 2.7 (sdlog)
	PEC-2008		Mean: 1.4; sd: 0.64		
	PEC-2008+		Mean: 2.1; sd: 0.96		
	PEC-2050-		Mean 0.52; sd: 0.24		
	PEC-2050		Mean: 1; sd: 0.48		
	PEC-2050+		Mean: 1.5; sd: 0.72		
	PEC-2100-		Mean: 0.23; sd: 0.07		
	PEC-2100		Mean: 0.47; sd: 0.14		
	PEC-2100+		Mean: 0.7; sd: 0.22		
	TWAC-2008-		Mean: 0.19; sd: 0.05		
	TWAC-2008		Mean: 0.38; sd: 0.1		
	TWAC-2008+		Mean: 0.56; sd: 0.15		
	TWAC-2050-		Mean: 0.12; sd: 0.04		
	TWAC-2050		Mean: 0.24; sd: 0.08		
	TWAC-2050+		Mean: 0.37; sd: 0.11		
	TWAC-2100-		Mean: 0.04; sd: 0.01		
	TWAC-2100		Mean: 0.09; sd: 0.05		
	TWAC-2100+		Mean: 0.13; sd: 0.04		

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Table S4 (*continued*)

Compound	Scenarios	Exposure distribution		Effect distribution	
		Type	Parameters	Type	Parameters
Difenoconazole	PEC-2008-	Normal	Mean: 8.2; sd: 0.72	Log-normal	Ac: 5.4 (meanlog); 1.9 (sdlog); Chr: 2.5 (meanlog); 2.2 (sdlog)
	PEC-2008		Mean: 16; sd: 1.4		
	PEC-2008+		Mean: 26; sd: 2.2		
	PEC-2050-		Mean: 6.7; sd: 0.81		
	PEC-2050		Mean: 13; sd: 1.6		
	PEC-2050+		Mean: 21; sd: 2.5		
	PEC-2100-		Mean: 6.2; sd: 0.64		
	PEC-2100		Mean: 12; sd: 1.28		
	PEC-2100+		Mean: 19; sd: 2		
	TWAC-2008-		Mean: 0.92; sd: 0.11		
	TWAC-2008		Mean: 1.83; sd: 0.22		
	TWAC-2008+		Mean: 2.9; sd: 0.34		
	TWAC-2050-		Mean: 0.71; sd: 0.08		
	TWAC-2050		Mean: 1.4; sd: 0.15		
	TWAC-2050+		Mean: 2.2; sd: 0.24		
	TWAC-2100-		Mean: 0.71; sd: 0.05		
	TWAC-2100		Mean: 0.67; sd: 0.06		
	TWAC-2100+		Mean: 2.2; sd: 0.16		
Imazamox	PEC-2008-	Normal	Mean: 1.8; sd: 0.59	Log-normal	Ac: 6.7 (meanlog); 3 (sdlog); Chr: 3.8 (meanlog); 2.2 (sdlog)
	PEC-2008		Mean: 2.4; sd: 0.79		
	PEC-2008+		Mean: 3.6; sd: 1.1		
	PEC-2050-		Mean: 1.8; sd: 0.55		
	PEC-2050		Mean: 2.4; sd: 0.73		
	PEC-2050+		Mean: 3.6; sd: 1.1		
	PEC-2100-		Mean: 1.7; sd: 0.53		
	PEC-2100		Mean: 2.3; sd: 0.71		
	PEC-2100+		Mean: 3.4; sd: 1		
	TWAC-2008-		Mean: 1.6; sd: 0.68		
	TWAC-2008		Mean: 2.1; sd: 0.83		
	TWAC-2008+		Mean: 3.2; sd: 1.2		
	TWAC-2050-		Mean: 1.5; sd: 0.58		
	TWAC-2050		Mean: 2; sd: 0.77		
	TWAC-2050+		Mean: 3.1; sd: 1.1		
	TWAC-2100-		Mean: 1.5; sd: 0.55		
	TWAC-2100		Mean: 2; sd: 0.74		
	TWAC-2100+		Mean: 3; sd: 1.1		
MCPA	PEC-2008-	Normal	Mean: 17; sd: 2.6	Log-normal	Ac: 9.9 (meanlog); 2.9 (sdlog); Chr: 6.6 (meanlog); 3 (sdlog)
	PEC-2008		Mean: 35; sd: 5.2		
	PEC-2008+		Mean: 52; sd: 7.9		
	PEC-2050-		Mean: 14; sd: 1.9		
	PEC-2050		Mean: 28; sd: 3.9		
	PEC-2050+		Mean: 42; sd: 5.9		
	PEC-2100-		Mean: 10; sd: 1.2		
	PEC-2100		Mean: 21; sd: 2.5		
	PEC-2100+		Mean: 32; sd: 3.8		
	TWAC-2008-		Mean: 11; sd: 3.5		
	TWAC-2008		Mean: 22; sd: 7		
	TWAC-2008+		Mean: 34; sd: 10		
	TWAC-2050-		Mean: 7.7; sd: 2.2		
	TWAC-2050		Mean: 15; sd: 4.4		
	TWAC-2050+		Mean: 23; sd: 6.6		
	TWAC-2100-		Mean: 4.7; sd: 1.1		
	TWAC-2100		Mean: 9.4; sd: 2.3		
	TWAC-2100+		Mean: 14; sd: 3.5		
Penoxsulam	PEC-2008-	Normal	Mean: 0.34; sd: 0.06	Log-normal	Ac: 7.1 (meanlog); 3.8 (sdlog);Chr: 4.5 (meanlog); 3.4 (sdlog)
	PEC-2008		Mean: 0.68; sd: 0.13		
	PEC-2008+		Mean: 1; sd: 0.19		
	PEC-2050-		Mean: 0.32; sd: 0.07		
	PEC-2050		Mean: 0.65; sd: 0.13		
	PEC-2050+		Mean: 0.97; sd: 0.2		
	PEC-2100-		Mean: 0.27; sd: 0.04		
	PEC-2100		Mean: 0.53; sd: 0.08		
	PEC-2100+		Mean: 0.8; sd: 0.13		
	TWAC-2008-		Mean: 0.27; sd: 0.08		
	TWAC-2008		Mean: 0.54; sd: 0.17		
	TWAC-2008+		Mean: 0.81; sd: 0.25		
	TWAC-2050-		Mean: 0.26; sd: 0.08		
	TWAC-2050		Mean: 0.51; sd: 0.16		
	TWAC-2050+		Mean: 0.77; sd: 0.23		
	TWAC-2100-		Mean: 0.19; sd: 0.05		
	TWAC-2100		Mean: 0.37; sd: 0.1		
	TWAC-2100+		Mean: 0.56; sd: 0.15		

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Table S4 (*continued*)

Compound	Scenarios	Exposure distribution		Effect distribution	
		Type	Parameters	Type	Parameters
Propanil	PEC-2008-	Normal	Mean: 0.52; sd: 0.07	Log-normal	Ac: 7.8 (meanlog); 2.1 (sdlog); Chr: 3.4 (meanlog); 1.3 (sdlog)
	PEC-2008		Mean: 1; sd: 0.14		
	PEC-2008+		Mean: 1.5; sd: 0.22		
	PEC-2050-		Mean: 1.6; sd: 0.42		
	PEC-2050		Mean: 3.2; sd: 0.84		
	PEC-2050+		Mean: 4.8; sd: 1.2		
	PEC-2100-		Mean: 0.57; sd: 0.06		
	PEC-2100		Mean: 1.1; sd: 0.13		
	PEC-2100+		Mean: 1.7; sd: 0.19		
	TWAC-2008-		Mean: 0.1; sd: 0.01		
	TWAC-2008		Mean: 0.2; sd: 0.01		
	TWAC-2008+		Mean: 0.3; sd: 0.02		
	TWAC-2050-		Mean: 0.26; sd: 0.05		
	TWAC-2050		Mean: 0.52; sd: 0.11		
	TWAC-2050+		Mean: 0.77; sd: 0.16		
	TWAC-2100-		Mean: 0.09; sd: 0.01		
	TWAC-2100		Mean: 0.18; sd: 0.01		
	TWAC-2100+		Mean: 0.27; sd: 0.02		

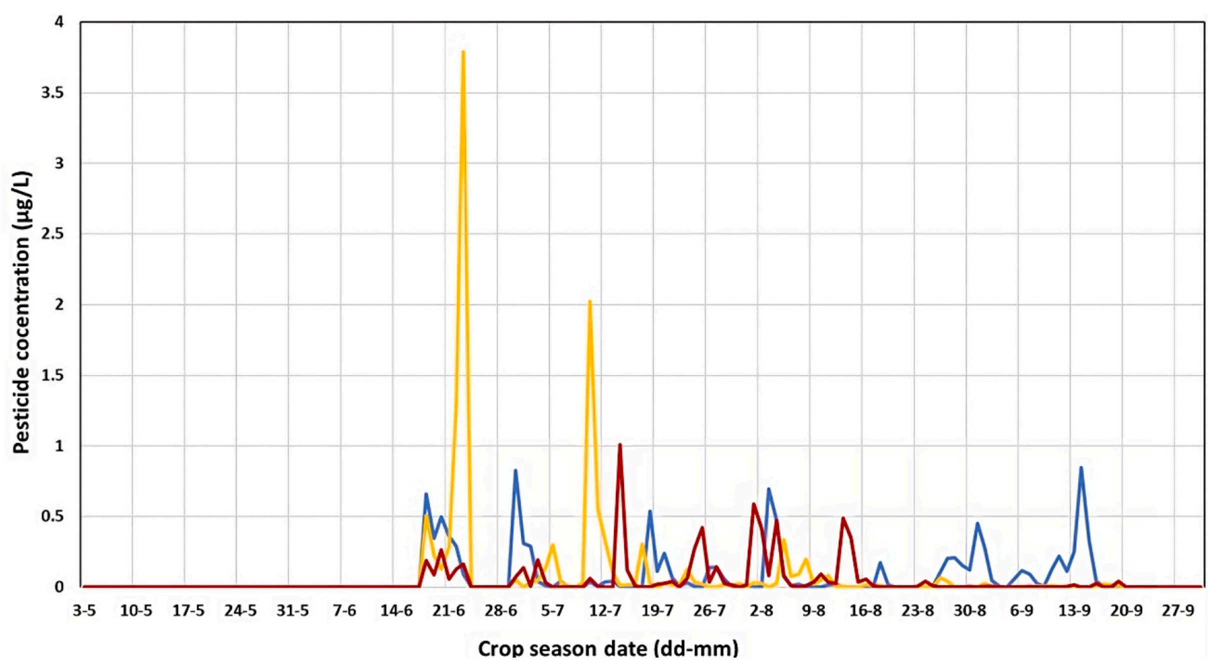

Fig. S3. Exposure concentration profile calculated with the RICEWQ model for the herbicide propanil in a given rice production cluster ("*02_Carrera_del_Saler0-2_0*") using the recommended application dose. Colors represent different climate scenarios: blue (2008), yellow (2050), red (2100). Concentration generally occur after rainfall events.