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Research article

Effect of climate change on the water quality of Mediterranean rivers and alternatives to improve its status

Diana Yaritza Dorado-Guerra[a,*], Javier Paredes-Arquiola[a], Miguel Ángel Pérez-Martín[a], Gerald Corzo-Pérez[b], Liliana Ríos-Rojas[c]

[a] Research Institute of Water and Environmental Engineering (IIAMA), Universitat Politècnica de València, Camino de Vera s/n, 46022 Valencia, Spain
[b] UNESCO-IHE Institute for Water Education, P.O. Box 3015, 2601DA Delft, the Netherlands
[c] Colombian Corporation for Agricultural Research (AGROSAVIA), Palmira Research Center, Palmira, Valle del Cauca, Colombia

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ABSTRACT

Surface water (SW) quality is particularly vulnerable to increased concentrations of nutrients, and this issue may be exacerbated by climate change. Knowledge of the effects of temperature and rainfall on SW quality is required to take the necessary measures to achieve good SW status in the future. To address this, the aims of this study were threefold: (1) to assess how a changing climate may alter the nitrate, ammonium, phosphorus and biological oxygen demand status (BOD_5) of SW; (2) assess the relationship between water quality and flow; and (3) simulate diffuse and point source pollution reduction scenarios in the Júcar River Basin District in the Mediterranean region. A regionalised long-term climate scenario was used following one Representative Concentration Pathway (RCP8.5) with the data incorporated into the coupling of hydrological and water quality models. According to these climate change scenarios, SW with poor nitrate, ammonium, phosphorus and BOD_5 status are expected to increase in the future by factors of 1.3, 1.9, 4 and 4, respectively. Furthermore, median ammonium and phosphorus concentration may be doubled in months with low flows. Additional measures are required to maintain current status in the water bodies, and it is necessary to reduce at least 25% of diffuse nitrate pollution, and 50% of point loads of ammonium, phosphorus, and BOD_5.

1. Introduction

Excessive nutrient inputs can have negative impacts on water bodies and aquatic ecosystems. These negative effects include eutrophication, biodiversity reduction, drinking water and groundwater (GW) contamination, an increase in the occurrence and intensity of harmful algal blooms, disruption of aquatic ecosystems, and oxygen depletion, all of which have been reviewed (Hilton et al., 2006; Mcdonald et al., 2016; Grizzetti et al., 2019). Anthropogenic activities are major sources of nutrients in European water bodies (EEA, 2018; Poikane et al., 2019). As human populations increase and industrial and agricultural activities expand, the load of nutrients released into water bodies also rises (Carvalho et al., 2019; Vigiak et al., 2021). For instance, a study carried out in Spain revealed that 43% of the total annual nitrogen input is accumulated in soil and water bodies, and the largest proportion of losses was associated with emissions from agriculture to water bodies (Mayor et al., 2023). A study in a semiarid region found that phosphorus chemical fertilisers and livestock were the two dominant sources of phosphorus input discovered in the water bodies (Yan et al., 2023).

Despite policies implemented to reduce nitrates and other pollutants, water quality in the European Union (EU) remains a cause for serious concern (Nikolaidis et al., 2022). According to the latest report from the European Environment Agency (EEA, 2018), 60% of the surface water (SW) bodies in the EU have poor ecological status, especially in central and north-western Europe, where agricultural practices are intensive and population density is high. Nikolaidis et al. (2022) found that 59% and 57% of the monitoring points in the SW bodies in the EU have concentrations above the limit marking good status for nitrate and phosphorus, respectively. According to the latest report on the status of the water bodies of the Júcar RBD (Confederación Hidrográfica del Júcar, 2022), 61% of the natural rivers achieve good physico-chemical status, while 22% of the rivers do not.

The effects of nutrient pollution on water bodies are expected to be exacerbated by climate change (Charlton et al., 2018), especially in coastal areas (Sinha et al., 2019; Temino-Boes et al., 2021). Other researchers have underlined that the transport of nutrients and their

* Corresponding author.
E-mail address: diadogue@doctor.upv.es (D.Y. Dorado-Guerra).

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permanence in streams will be modified in response to changes in rainfall, temperature, and hydrology (Trang et al., 2017; Whitehead et al., 2019). Higher temperatures and changes in nutrient concentrations can have severe impacts on the availability of water for human consumption and agriculture. This, coupled with increasing anthropogenic loads, may lead to significant impacts on water quality in the future (Huang et al., 2022; Yuan et al., 2023). Moreover, climate change is worsening these problems by exposing rivers to greater temperature and hydrological variability, increasing pollution levels, reducing the efficiency of natural purification processes and endangering aquatic ecosystems (Mirauda et al., 2021). In the face of these challenges, traditional methods of risk management are no longer adequate. The intersection of urbanisation and climate change is making rivers increasingly vulnerable, requiring holistic strategies capable of addressing both established and emerging threats (Oduor et al., 2023; Vagheei et al., 2023).

The Mediterranean coast is one of the most sensitive areas to climate change due to the expected decrease in average rainfall and water stress caused by current demand exceeding available resources (Serrano et al., 2020; Estrela-Segrelles et al., 2021). According to a study carried out on the effects of climate change in the Júcar River Basin District (RBD) (Pérez-Martín et al., 2022), in the future there will be a tendency towards less rainfall (20% RCP 8.5) and higher temperatures (up to 4 °C), resulting in lower annual water resources and soil moisture in the spring.

Nutrient transport depends on water and sediment flows, which are governed by local hydrology. According to Kamrath and Yuan (2023) and Yin et al. (2023), nutrient fluxes are strongly correlated with hydrometeorological conditions. Mishra et al. (2021) and Fabian et al. (2023) summarised the impacts of extreme events on water quality conducted around the world, underlining the difficulties in understanding the causal mechanisms and the degradation of water quality under extreme climatic conditions, as this depends mainly on the spatio-temporal interaction of each basin. Therefore, predicting water quality changes in response to climate change is a challenge. Furthermore, the literature review conducted in this study did not find any research relating nutrient concentrations to flow in Mediterranean basins under the effects of climate change in the far future.

The focus of this work is based on the lack of knowledge of the impacts of climate change on water quality and the relationship of hydrometeorological conditions with nutrient concentrations in Mediterranean basins, such as the Júcar RBD, in the far future. The Júcar RBD is situated on the border between the humid climate of the northern interior and the arid climate of the south. It encompasses basins characterized by varying degrees of groundwater influence, resulting in a diverse range of scenarios. This RBD covers multiple instances of the Mediterranean climate. The applied methodology is extended to nine river basins with differing typologies. Furthermore, the Júcar RBD has been chosen as one of the pilot basins for implementing the Water Framework Directive in Europe (Estrela et al., 2004). Apart from monitoring stations, it is crucial to be able to predict possible future loads and changes in nutrient status and water flow through climate change. This makes it possible to analyse how pressures will affect water bodies, thereby enabling measures to be put in place to help achieve good status for water bodies. The first aim of this study is to include temperature and rainfall variations in the far future in the coupling of hydrological and water quality models for the Júcar RBD in order to assess how a changing climate may alter the nitrate, ammonium, phosphorus and biological oxygen demand status (BOD_5) of SW. The second aim is to assess how decreasing diffuse pollution (DP) and point pollution (PP) loads in conjunction with climate change will affect the status of water quality in the far future. Finally, the last objective of this study is to understand the relationship between water quality and flow in the baseline and under climate change. The contributions of this study include its comprehensive assessment of the potential impacts of climate change on surface water quality, its quantification of the projected changes, its exploration of the relationships between flow and water quality, and its proposal of pollution reduction scenarios to mitigate the adverse effects of climate change in the Júcar RBD.

2. Material and methods

2.1. Case study

Geographically, the Júcar RBD is located in the centre-east of the Iberian Peninsula (Spain), with an area of 42,735 km^2. The Júcar RBD is constituted by the grouping of nine river basins – 1) Cenia-Maestrazgo, 2) Mijares-Plana de Castellón, 3) Palancia y los Valles, 4) Turia, 5) Júcar, 6) Serpis, 7) Marina Alta, 8) Marina Baja, and 9) Vinalopó-Alacantí (hereafter referred to by its first name) – which drain into the Mediterranean Sea (Fig. 1a). The main climatic parameters for the period 1940 to 1980 include the following: mean annual rainfall of 534 mm, a mean annual temperature of 13.4 °C, and potential evapotranspiration of 954 mm/year. Recent climate evolution for the period 1980–2020 shows a reduction in mean annual rainfall to 492 mm, an increase of 0.7 °C in mean temperature, and 20 mm/year in potential evapotranspiration. These changes have led to a decrease in the annual amount of snowfall and have reduced the district's natural resources since 1980. Available data show a trend towards lower rainfall and higher temperatures. Natural inflows have decreased from 3.4 km^3/year to 2.84 km^3/year, a reduction of 17%, spread over the whole year (Pérez-Martín et al., 2022).

According to the latest report on the pressures, impacts and risks to water bodies of the Júcar RBD (Confederación Hidrográfica del Júcar, 2023), urban wastewater and spillways (storm water discharges) affect 47% and 49%, respectively, of the total SW bodies in the district and to a lesser extent industrial plants not subject to integrated environmental authorisation. The treatment plants in Valencia, Albacete, and Ribera Alta (50,000–100,000 inhabitants) generate the largest volume of wastewater discharges (40 H m^3/year, Fig. 1a).

The description of the current land cover (Fig. 1b) was made using the Corine Land Cover database (CLC, 2018). In the Jucar RBD, 49% of the land is occupied by forest areas and open spaces (2,362,448 ha), whereas agriculture (1,749,561 ha) represents 31% of land use. The most predominant crops are olive trees, fruit trees, and vineyards, which are located in the coastal areas, the middle and upper basins of Júcar and Vinalopó and the rainfed crops in the upper basins (Fig. 1b). As a result, 91% of SW bodies are under pressure from nitrogen loading (Confederación Hidrográfica del Júcar, 2023). In a previous study it was reported that the SW bodies with the highest nitrate concentration were in irrigated agricultural areas (Dorado-Guerra et al., 2021). This is because the water to supply agricultural water demands comes from GW (40%), and SW combined with GW (mixed, 38%), and the nitrate concentration in the permeable aquifers located in the coastal zone is above the threshold (Confederación Hidrográfica del Júcar, 2022). Artificial surfaces (141,029 ha) occupy 3% of the total land area of the Júcar RBD; however, in Marina Alta, Marina Baja and Vinalopó the percentage of artificial surface with respect to the total area of the basin increases to 15%, 10% and 9%, respectively.

Climate change scenarios indicate a progressive increase in air temperature in the long term (2070–2100) by up to 4 °C. Mean annual rainfall will decrease over the century, reaching a reduction of 20% RCP8.5 b y the end of the century. The combination of both factors results in a 36% reduction of water resources in the long term under the RCP8.5 scenario. In addition, there will be an increase in the occurrence of droughts and in maximum hourly precipitation (Pérez-Martín et al., 2022).

2.2. Methodology

The phases to develop this research are shown in Fig. 2, which include the following: 1) coupling hydrological and water quality models using climate, hydrological, hydrogeological, and anthropogenic

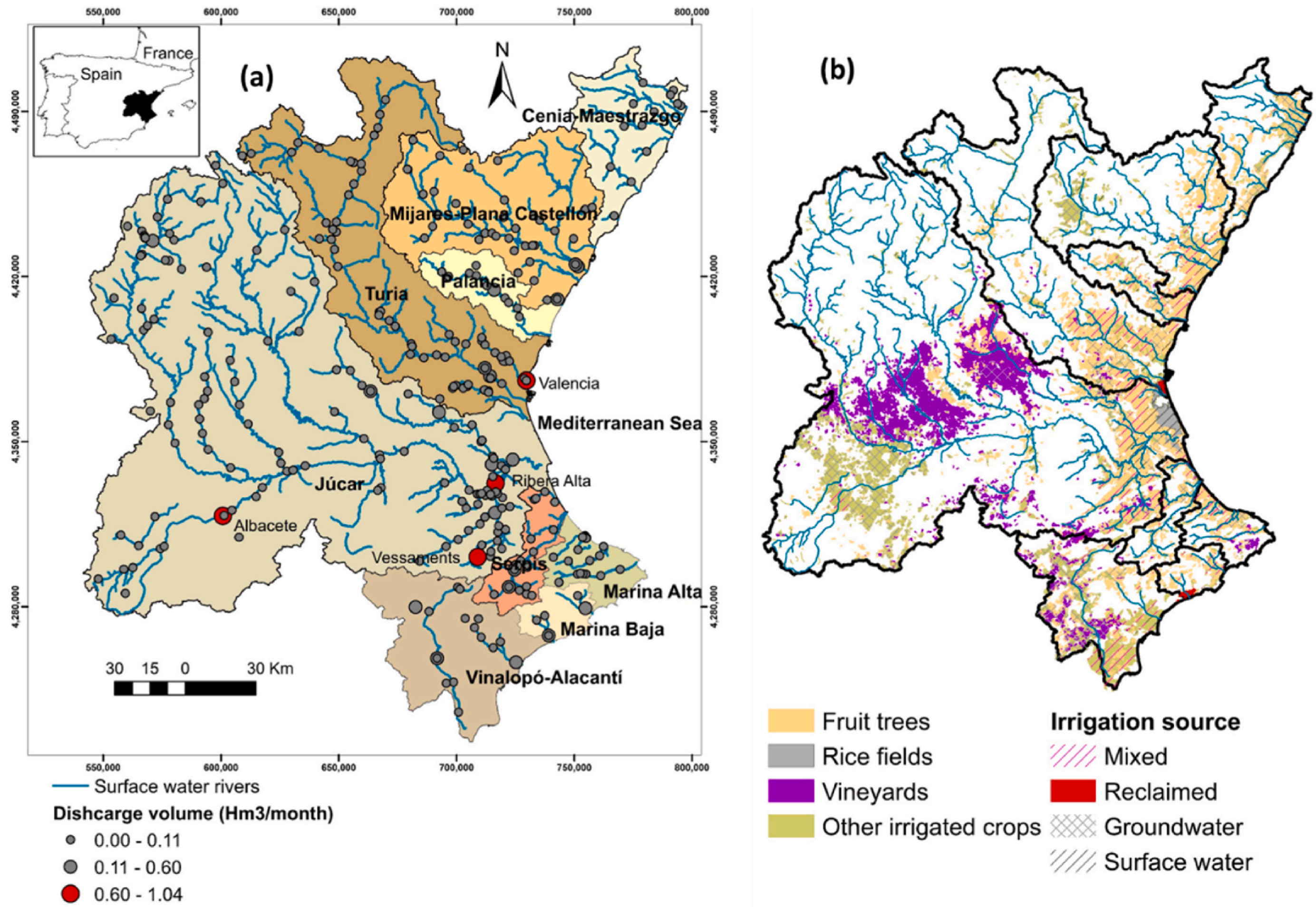

Fig. 1. (a) Location of the surface water hydrographic network of the Júcar RBD, and the volume of point discharges (b) Agricultural area and irrigation sources.

data from the study area; 2) generating a long-term scenario (2070–2100) following 8.5RCP that includes future temperature and rainfall anomalies in the models; 3) producing new water quality and quantity modelling using the projected changes; 4) plotting future scenarios with percentage of reduction of DP and PP; 5) estimating nutrient and BDO_5 status in SW under climate change and scenarios of reduction of pollution in the far future; and 6) establishing the relationship between water quality and quantity in the baseline and under climate change in the far future.

2.2.1. Coupling hydrological and water quality models

The coupling of the two models is conducted to integrate aspects of catchment hydrological behaviour, river-aquifer interaction and water quality assessment. A previous study used the coupling of models to simulate flow and nitrate concentration and found good model performance (Dorado-Guerra et al., 2021).

PATRICAL (Pérez-Martín et al., 2014, 2016) is a conceptual model used for distributed hydrological simulation and calculating water quality in SW and GW bodies. The water quality component of PATRICAL simulates the transport of nitrates from DP through the hydrological cycle throughout the catchment. Input variables of the model are the irrigation returns that recharge the aquifers, GW extractions, lateral transfers between aquifers, water movement through the river network, the evolution of the average piezometry of the aquifers, and SW-GW interactions. For further details on the formulation of the model and the parameters used, refer to Pérez-Martín et al. (2014).

The RREA model estimates the concentration in SW bodies of pollutants that can be modelled with first order kinetics. The model is based on four hypotheses: 1) that degradation of the pollutant happens according to first-order kinetics; 2) that the load of each mass can be calculated according to the discharges received by each mass; 3) that the mass flow is the flow generated in the sub-basin, taking into account the flow rate extracted in each body of water; and 4) mass and flow is accumulated by flow order. A more extensive description of RREA is found in Paredes-Arquiola (2021).

PATRICAL replicates the river-aquifer relationship and a portion of the altered hydrological cycle, as it does not incorporate reservoir management or the corresponding changes to the flow regime. The two models are complementary, with RREA enabling the integration of reservoir management and regulation, agricultural and urban demands, as well as alterations in the effects of the flow regime. The cumulative monthly time series of river flows, and total loads of nitrate from diffuse agricultural pollution to surface waters, as obtained in PATRICAL, constitute the principal inputs for RREA; therefore, the simulation period is the same for both models. A set of algorithms was implemented in the Python software (Van Rossum, 1999) to facilitate the processes of load and input deaccumulation and to transform the outputs of PATRICAL into the same format employed by RREA. The output of the RREA are the monthly time series of streamflow, nutrients and BOD_5 concentration in the water bodies under conditions altered by human activities. The overall schematic illustrating the coupling of the two models is presented in Fig. 3.

2.2.2. Dataset

Rainfall and air temperature data series in the historical studied period (1980–2018) have been obtained from AEMET (the State

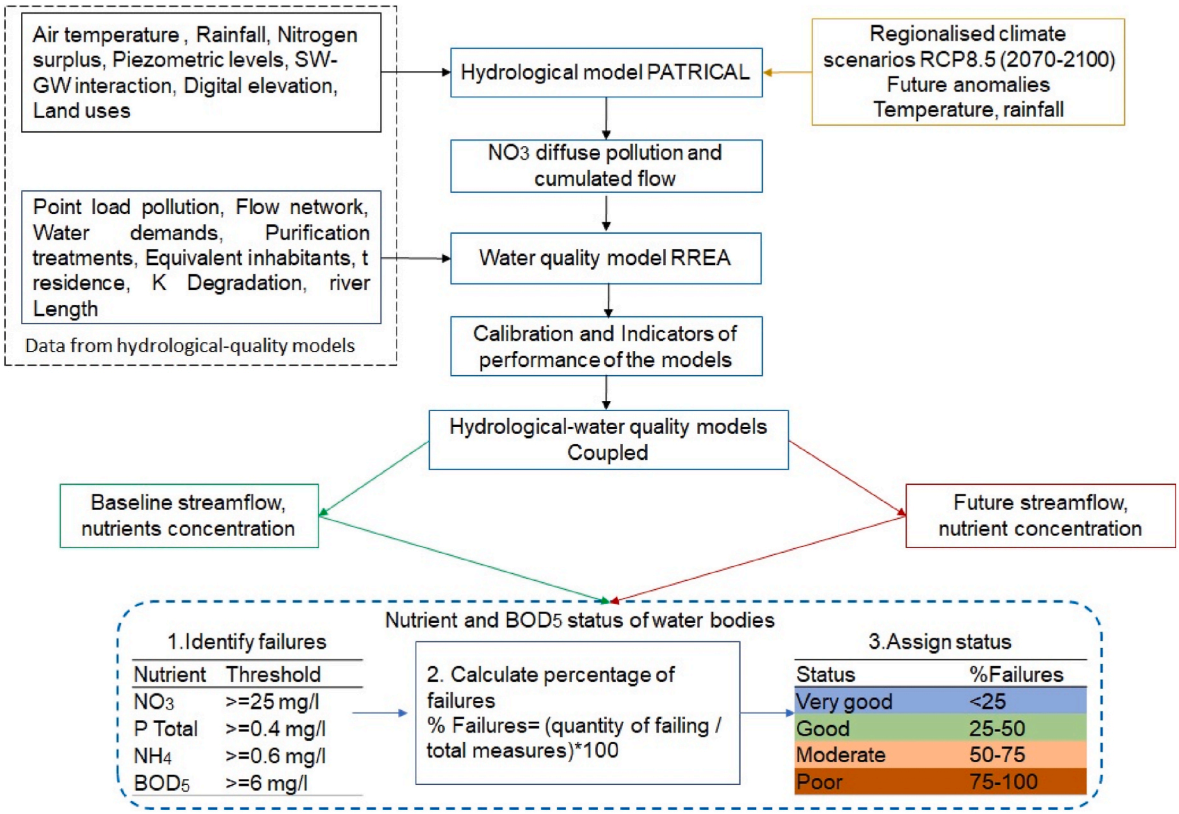

Fig. 2. Methodological framework for water quality assessment under climate change scenario.

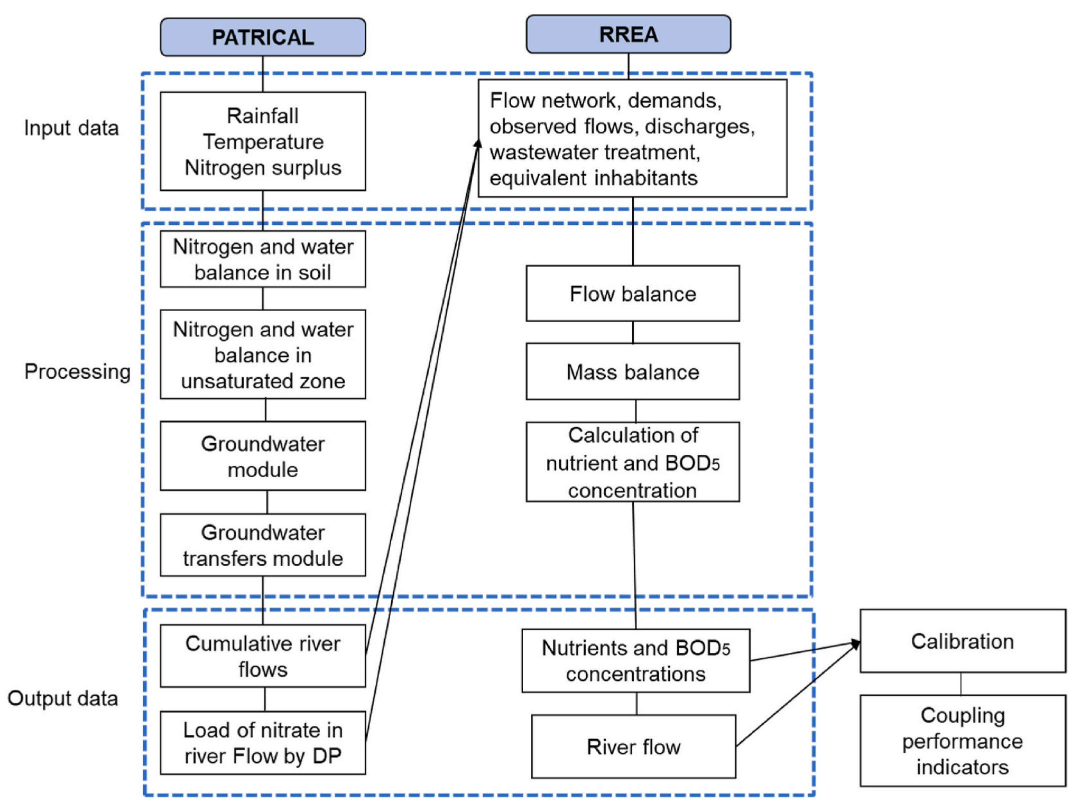

Fig. 3. Process of coupling the two models.

Meteorological Agency in Spain) (Peral García et al., 2021). SW and GW hydrographic network, the location of the physical infrastructure, the water supply and demands used in the models come from the Water Information System for the Jucar RBD (SIA Júcar in Spanish: aps. chj. es/siajucar/, accessed on April 2020).

Nitrate concentration was modelled including both PP and DP, while ammonium, phosphorus, and BOD_5 concentrations were modelled with point source pollution. According to a previous study in the area (Suárez-Almiñana et al., 2021), the RREA model provides a good fit for ammonium, phosphorus and BOD_5 concentrations in surface waters when only the point source load is considered. Information on point source discharges to SW bodies (volume, purification treatments, equivalent inhabitants) was provided by SIA Júcar and the National Dumping Census (miteco.gob.es/es/agua/temas/concesiones-y-autorizaciones/vertidos-de-aguas-residuales/censo-vertidos/, accessed on May 2021). On the other hand, the surplus of nitrogen in the soil comes from the municipal balance and the evolution of overall nitrogen levels in Spain (MAPA and y A, 2018; Pérez-Martín et al., 2014).

The nitrate, ammonium, phosphorus, and BOD_5 concentrations, streamflow in SW and piezometric levels were measured by the Júcar RBD authority and the data were available from the SIA Júcar (aps.chj. es/siajucar/, accessed on April 2020). The Júcar RBD water quality sampling network consists of 514 gauging stations distributed throughout its hydrographic network. Sampling is carried out on a monthly basis, and data has been available from 1990 to the present.

2.2.3. Performance of the coupling of the models

In order to evaluate the performance of the coupling of hydrological and quality models to predict nutrients and BOD_5 concentration in the Júcar RBD, a confusion matrix was used (Wilks, 2007). This method compares the simulated concentration with the corresponding observed values in the baseline, considering the threshold allowed in the Spanish regulation for each of the parameters.

Four indicators were measured: 1) the accuracy (ACC), which evaluates the model's performance in properly reproducing an event; (2) the bias, which is the ratio of the simulated mean and observed mean, with a best value of 1, and a bias value less than 1 showing the model underestimates the concentration of nutrients and values greater than 1 meaning overestimation; (3) the success ratio (SR), which gives information on the rate of water bodies with a concentration below the allowed threshold correctly identified in the simulation; and (4) the specificity (SP), which is the rate of water bodies with a concentration above the allowed threshold correctly identified in the simulation. ACC, SR and SP range from 0 to 1, and 1 is the best value. The process of producing the confusion matrix and the four indicators was described in more detail in Dorado-Guerra et al. (2021).

2.2.4. Scenario of climate change

This study includes only the spatial variability of monthly rainfall and temperature as obtained by the Spanish State Meteorological Agency (AEMET, in Spanish) in the third delivery of regional projections (Amblar-Francés et al., 2017). According to Amblar-Francés et al. (2018), the AEMET strategy for generating climate change projections consists of applying two statistical regionalization methods (analogy and regression) to the general circulation models used in the Fifth Assessment Report (AR5) and to the regionalised dynamic projections of the EURO-CORDEX project. The scenario considered was RCP8.5 (Representative Concentration Pathways) in the long term (2070–2100), which corresponded to a radiative forcing of 8.5 W/m^2 at the end of the 21st century and associated CO_2 levels exceeding 1000 ppm at the end of the century. The RCP8.5 scenario assumes that greenhouse gas emissions will continue to increase throughout this century, with peak emissions at the end of this century or early in the next. Rainfall and temperature variations for the selected scenario were downloaded from the AdapteCCa platform (escenarios.adaptecca.es, accessed in February 2021).

The bias correction was generated using the Delta Change approach (Räisänen and Räty, 2013), which meant that the model anomaly was added to the actual historical monthly data. The model anomaly is defined as the difference between the monthly data of the simulated scenario and the monthly data of the model control period. The observed data were historical data from the study area (1980–2018), used to develop the periods of future simulations according to the scenario. The Delta Change approach was applied to the observed baseline of study area to obtain a corrected future series, which allowed reducing uncertainty. This technique has been applied in other studies (Pardo-Igúzquiza et al., 2019; Rivadeneira Vera et al., 2020).

2.2.5. Scenarios of reduction of diffuse pollution and point pollution in the long-term (2070–2100)

Measures to reduce the concentration of pollutants in water include improving water treatment in water treatment plants and reducing the application of nutrients or improving fertilisation methods in agriculture. In order to understand the possible effect of these measures, four scenarios with percent reductions (25%,50%,75%,100%) in DP and PP were simulated for each nutrient studied. These scenarios have been considered in order to cover all the variability of the load received and to be able to determine whether the pollution is due to point or diffuse load. The reduction to zero of the point or diffuse loads is a theoretical scenario to identify the weight of each source of pollution in the river basin and to know, for each water body and each pollutant, whether the priority is to act on point or diffuse pollution. The simulation results of these models are used by river basin authorities to prioritise the actions needed to prevent the effects of climate change on surface water bodies.

2.2.6. Calculation of failure rate and nutrient status

The biological, chemical and hydromorphological status is used to determine whether an aquatic ecosystem is at risk. The maximum thresholds for each of the modelled pollutants and the reference limits for the classification of the ecological status of SW bodies (Fig. 2) are in accordance with Royal Decree 817/2015, which transposes into Spanish law the provisions of Directive (2000)/60/EC of the European Parliament, establishing a framework for community action in the field of water policy.

When the concentration of the pollutant is above the limit, the analysed water body is considered to be "failing". The percentage of failures is then calculated as a percentage of the total number of measurements in each water body. The nutrient status of the water body is assigned according to the percentage obtained of failures, and this process is shown in Fig. 2.

2.2.7. Relationship between streamflow and water quality

To understand the relationship between streamflow and water quality, the threshold method was used. This approach identifies droughts and total runoff as periods during which flow values fall below or above predefined threshold levels. This method describes drought and runoff in terms of duration and deficit or excess volume (Tallaksen et al., 2004).

In order to assess the behaviour of the physicochemical parameters in low flow, standard, and high flow, the threshold levels selected in this study corresponded to the 20th percentile (P20) of the monthly streamflow in low flow, and to the 80th percentile (P80) in high flow. The standard periods were between the two thresholds (P20–P80), and P20 and P80 values were calculated for each basin at baseline and under climate change. This method has been applied in other studies (Van Loon, 2015; Peña-Guerrero et al., 2020).

3. Results

3.1. Performance of the coupling of models

The water bodies in good (below the threshold) and poor (above the

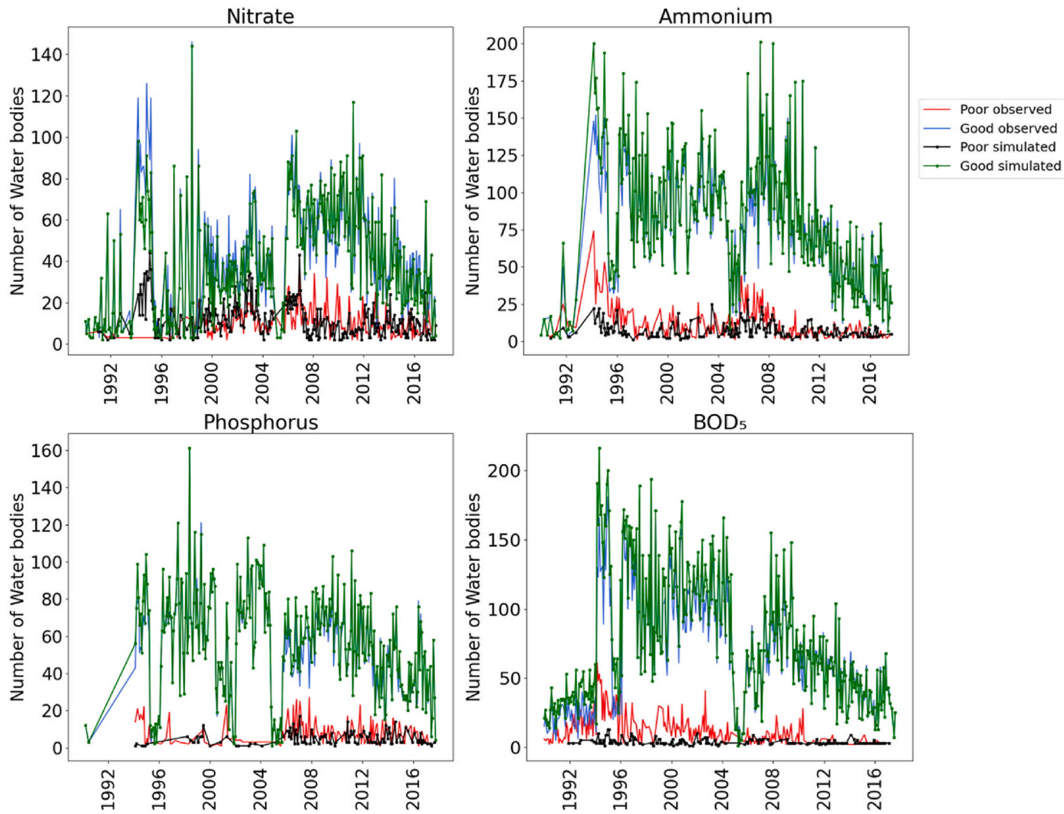

Fig. 4. Water bodies in good or poor condition for nitrate, ammonium, phosphorus and BOD_5 in the observed and simulated dataset for the period 1990–2018.

threshold) condition for observed and simulated pollutants for the period 1990–2018 are compared in Fig. 4. The predicted pollutant condition of surface waters aligns well with the reported values, except for the early years of the time series, wherein the simulated data do not effectively represent water bodies in poor condition. The periods with limited reports can be attributed to droughts (1991–1996, 1997–2001, 2004–2007, 2013–2014; Confederación Hidrográfica del Júcar, 2018), particularly notable in 2005 due to significantly low rainfall. During these intervals, many intermittent streams may not have contained water at the time of sampling. The observed time series of ammonium and BOD_5 indicates a decline in the number of water bodies in poor condition over time.

The seasonal variation of surface water bodies in poor and good condition for nitrate, ammonium, phosphorus and BOD_5 in the downstream area of the Jucar River for the period 2007–2018 is shown in Fig. 5. Overall, the simulated dataset captures the seasonal variation observed in the dataset for all four pollutants. In both the observed and simulated datasets, the count of water bodies with a good nitrate condition is greater during summer when contrasted with winter and spring. During autumn, the data displays significant variability. Conversely, the seasonal pattern for water bodies with poor nitrate condition differs from that of those with good condition, with the highest count occurring in winter and the lowest in summer.

The concentration of ammonium, phosphorus and BOD_5 in the surface water bodies downstream of the Júcar River Basin is below the threshold for poor condition for each of these pollutants, resulting in the absence of water bodies in poor condition (Fig. 5). For ammonium in the observed and simulated datasets, the mean number of water bodies in good condition is higher in spring compared to autumn, while in winter and summer the means are similar. The mean values of water bodies with good phosphorus condition are slightly similar between seasons, but the variability of the data is high in spring and winter. In the case of BOD_5, the mean count of water masses in good condition is higher in winter than in summer. In the summer period there is a remarkable degree of variability in the data. The high variability and seasonal variation in the number of water bodies with good ammonium, phosphorus and BOD_5 condition is also influenced by the different number of samples taken from one season to another.

The indices calculated using the confusion matrix are shown in Fig. 6. The accuracy of the models for classifying nitrate status are 0.81 in the Júcar RBD, ranging from 0.64 to 0.99 in the catchments. Cenia and Marina Alta were the basin with least accuracy, while Mijares, Palancia, Turia and Marina Baja were close to optimal. The BIAS indicator reported that the nitrate status in the Mijares, Palancia, Turia, Júcar, Marina Alta and Marina Baja areas was unbiased or slightly biased. Serpis and Vinalopó obtained values above the optimum, indicating that the models overestimated the nitrate concentration, while in Cenia the nitrate concentration was underestimated. The SR indicator shows the rate of SW bodies were correctly simulated with the concentration below the allowable threshold (True Positive, TP). SR ranged from 0.58 to 0.99, while the highest SR were obtained in Cenia, Mijares, Palancia, Turia, Júcar, Marina Alta and Marina Baja. On the other hand, the lowest value was obtained in Vinalopó, which was because some water bodies in poor status in the observed data set were simulated as being in good status, and there was a low TP rate. However, the SP indicator showed the rate of SW bodies was correctly simulated with the concentration above the allowable threshold (True Negative, TN). Cenia, Marina Baja and Vinalopó recorded the highest SP values; therefore, in these basins the water bodies above the threshold were correctly classified. The SP indicator for Vinalopó was considerably improved compared to the previous study (Dorado-Guerra et al., 2021). In Mijares and Palancia the SP values were very low; however, the other indicators were not affected because the number of bodies with nitrate concentrations above the threshold was very low with respect to the total number of bodies in the basin.

The accuracy of the models for classifying ammonium status was 0.88 in the Júcar RBD, with the catchments ranging from 0.75 to 1.0. Cenia, Mijares, Palancia, Turia, Júcar, Marina Alta, and Marina Baja

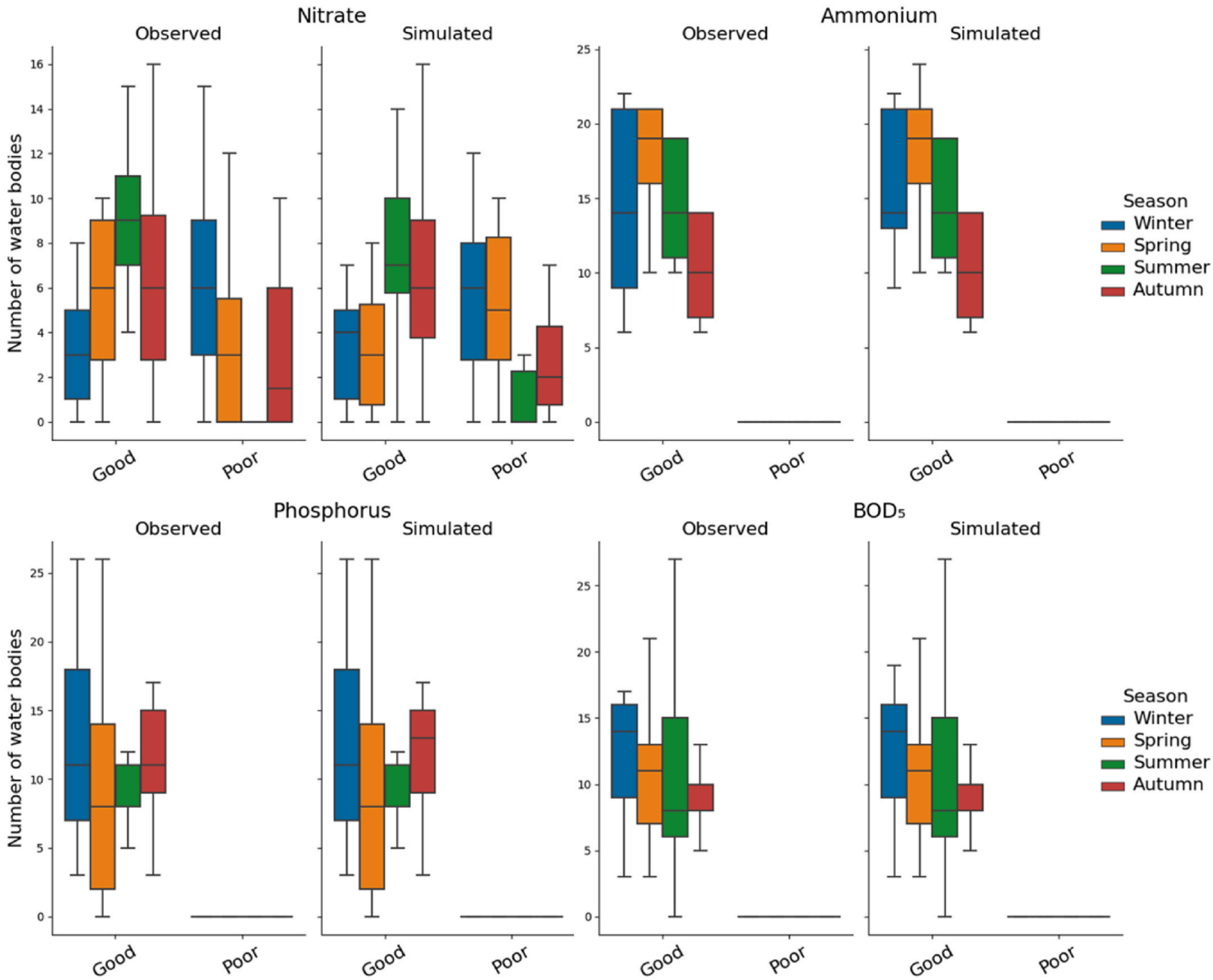

Fig. 5. Seasonal variation of surface water bodies in poor and good condition for nitrate, ammonium, phosphorus and BOD_5 in the downstream area of the Jucar River for the period 2007–2018.

were close to optimal. The BIAS indicator reported that the ammonium status in all basins was close to optimal. SR ranged from 0.73 to 1.0; therefore, SW bodies with ammonium concentration below the threshold were properly classified in the simulation. Additionally, the SP indicator showed a high rate of TN in Mijares and Vinalopó and hence in these basins the water bodies above the threshold were correctly classified. In Marina Baja the SP values were very low; however, the rest of the indicators were not affected, because there were fewer water bodies with poor status than water bodies with good status. In Cenia, Palancia and Marina Alta the SP value was zero because there were no SW bodies with ammonium concentration above the threshold.

For phosphorus, the accuracy of the models for classifying the status in the Júcar RBD was 0.92. The results of the phosphorus classification confusion matrix were similar to those of ammonium. The BIAS indicator reported that the ammonium status in all basins was close to optimal, with the exception of Vinalopó. In this basin, the phosphorus concentration was slightly underestimated. SR ranged from 0.71 to 1.00, similar to ammonium. The SP indicator showed a high rate of TN in Mijares, Turia, and Vinalopó. In contrast to the ammonium results, the SP in Marina Baja was high. For the same reason as with the ammonium findings, the SP value was zero in Cenia, Palancia and Marina Alta.

For BOD_5, the accuracy of the models for classifying the status in the Júcar RBD was 0.83. The results of the BIAS indicator were similar to those of phosphorus, with all the basins close to the optimum value – with the exception of Vinalopó, for the same reason as mentioned above. SR ranged from 0.91 to 1.00; therefore, SW bodies with BOD_5 concentrations below the threshold were properly classified in the simulation. The SP indicator showed a high rate of TN in Serpis and Vinalopó. For the same reason as with ammonium and phosphorus, the SP value was zero in Cenia, Palancia and Marina Alta. In Marina Baja, Turia and Mijares the SP values were very low; however, the rest of the indicators were not affected, with conditions similar to those found for nitrates and ammonium.

In general, the models reliably represented the status of nutrients and organic elements. The concentration of ammonium, phosphorus, and BOD_5 in the Cenia, Palancia, and Marian Alta RBs is shown as below the threshold in the observed and simulated data set.

3.2. Effect of climate change on nutrients and BOD_5 status

Fig. 7 shows the baseline and far future changes according to the RCP8.5 scenario for each nutrient and BOD_5. For the nitrate in the baseline, 82% of the water bodies were in good status, while 12% had a moderate risk to be in poor status, and 6% were in poor status. In the far

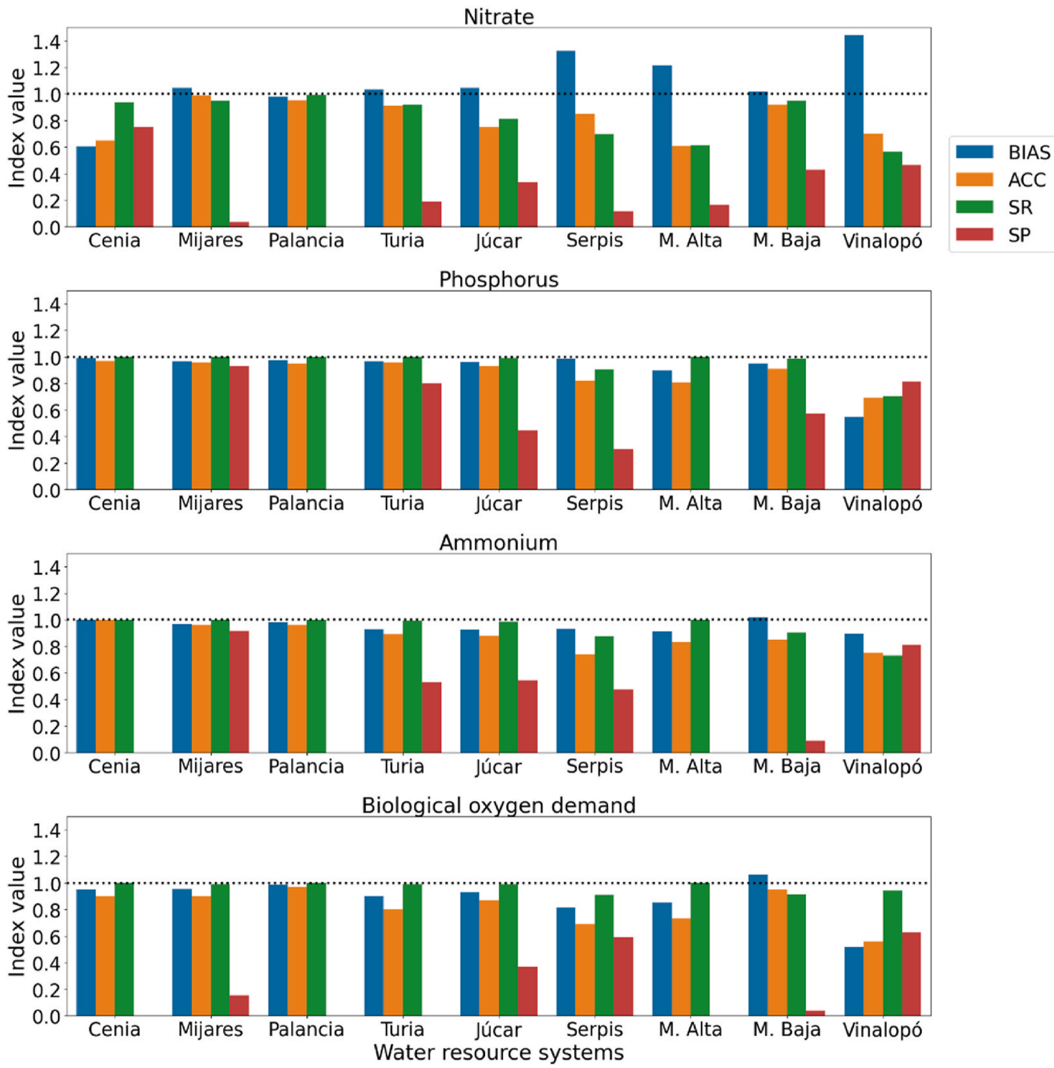

Fig. 6. Performance measures of the coupling of the models (ACC: Accuracy; SR: Success Ratio; SP: Specificity).

future, climate change was expected to increase the water bodies in poor status to 8%, which meant that more than 75% of the time the nitrate concentration in these water bodies would be above the threshold. Moreover, 12% and 5% of water bodies with good and moderate status at baseline, respectively, would be in poor status due to climate change. There were more sub-basins with a nitrate concentration leading to poor status than with the other nutrients and BOD_5. The main nitrate pollution issues were located in the coastal area of the district, and the middle zone of the Júcar and Vinalopó rivers. This pollution area was maintained in the baseline and with climate change. The source of pollution problems were shown to be agricultural areas with irrigation (Figs. 7 and 1b), which is in agreement with previous studies in the region (Dorado-Guerra et al., 2021).

Climate change will affect ammonium status in the far future by increasing poor water bodies by roughly double compared to the baseline. Moreover, 50% of water bodies with moderate status at baseline will be in poor status under climate change. The main ammonium pollution issues were located near wastewater treatment plants (WWTP) in urban areas with the highest point loads (Figs. 7 and 1a), and affected areas at baseline and with climate change were the same.

Phosphorus status will be more affected by climate change, as water bodies in poor status increase fourfold compared to the baseline. In addition, 55% and 30% of water bodies with moderate and good status at baseline will be in poor status under climate change. As with ammonium, phosphorus pollution zones were located near WWTPs with the highest point loads (Figs. 7 and 1a).

For BOD_5, at the baseline, 98.8% of water bodies were in good status, while 0.9% were at moderate risk of poor status and 0.3% were in poor status. Although the percentage of water bodies in poor status was very low, climate change increases this percentage fourfold. The affected areas with BOD_5 concentrations above the threshold coincided with the areas affected by ammonium and phosphorus.

The water bodies with the greatest environmental problems were tributaries or intermittent rivers. In general, the main watercourses, which had high flows, did not present an environmental risk for the pollutants assessed. There were specific areas in the district that require special attention because they had problems with all the nutrients and BOD_5: the Vinalopó RB, with the exception of the upstream, the midstream and downstream of Júcar, and the downstream of Turia and Mijares (Fig. 7).

3.3. Scenarios of reduction of diffuse pollution and point loads in the long-term (2070–2100)

Once the far future rainfall and temperature variations under RCP8.5 pathway were included in the models, different scenarios with reductions of DP and PP were built (Fig. 8). DP scenarios were only applied to nitrate and PP scenarios for all nutrients and BOD_5.

For nitrate, the scenarios of reduction of diffuse loads DP75, DP50, DP25 and DP0, represented a decrease in the water bodies in poor status

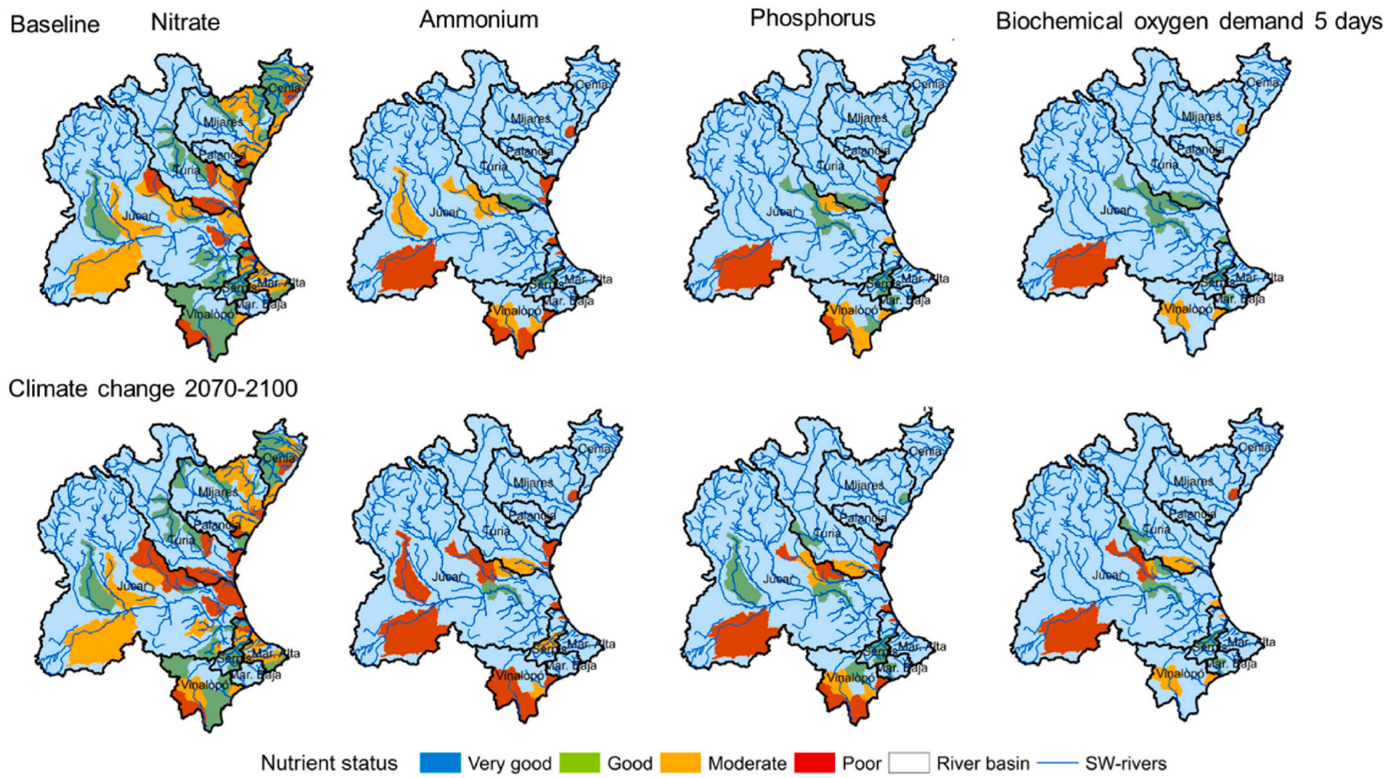

Fig. 7. Baseline and far future changes in status under the RCP8.5 pathway for each nutrient and BOD_5 status of SW bodies in the Júcar RBD.

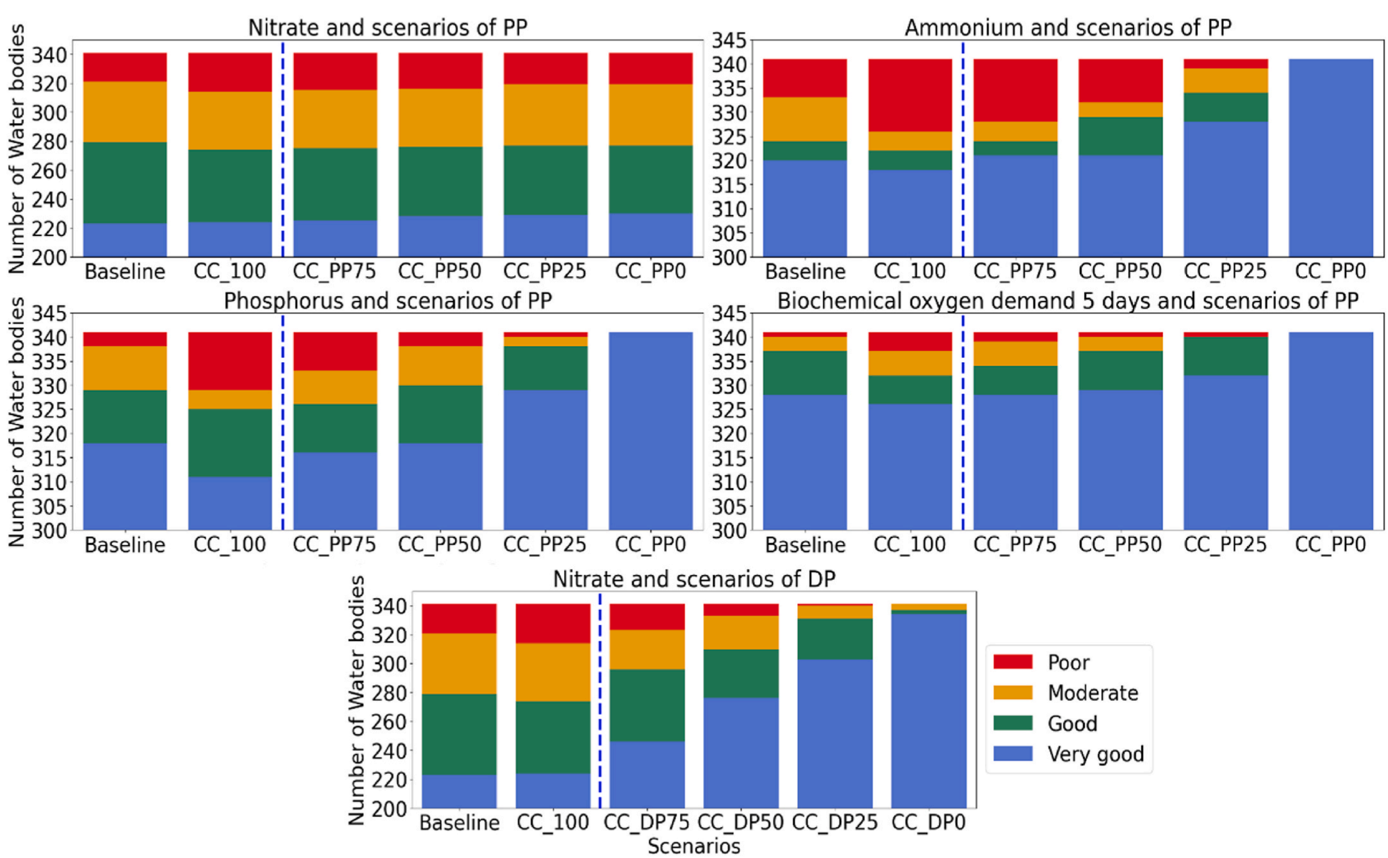

Fig. 8. Effects of different scenarios of reductions of diffuse and point pollution in the far future (2070–2100) according to the RCP8.5 pathway on the nutrients and BOD_5 status of SW bodies in the Júcar RBD. The scenarios of point pollution (PP) are 100%, 75%, 50%, 25% and 0% of loads corresponding to the abbreviations CC_100, CC_PP75, CC_PP50, CC_PP25, CC_PP0. The scenarios of diffuse pollution (DP) are 100%, 75%, 50%, 25% and 0% of loads corresponding to the abbreviations CC_100, CC_DP75, CC_DP50, CC_DP25, CC_DP0. To the right of the dashed lines are the alternatives for reducing point and diffuse loads.

around 33%, 70%, 96%, and 100%, respectively (Fig. 8). Reducing the DP load by 25% (DP75) would result in a number of water bodies in poor status in the far future similar to the baseline. The DP25 scenario notably improved the number of water bodies in good status from 80% to 97%. On the other hand, even if the reduction of DP were 100% (DP0), 1% of water bodies were expected to have a moderate risk of poor status. This was because in some streams in the district there was a high-to-medium nitrate transfer from the aquifers (Dorado-Guerra et al., 2021), and this interaction was represented in the models. In addition, the point load also played a role. The scenarios of reduction of point loads PP75, PP50, PP25 and PP0 represented a decrease in the water bodies in poor nitrate status around 4%, 7%, 19%, and 19%, respectively (Fig. 8). Reducing the point loads of nitrate by between 75% and 50% did not represent significant change in the nitrate status due to the main source of nitrate pollution being diffuse load. Therefore, to obtain 19% fewer water bodies in poor nitrate status, it would be necessary to reduce 75% of the

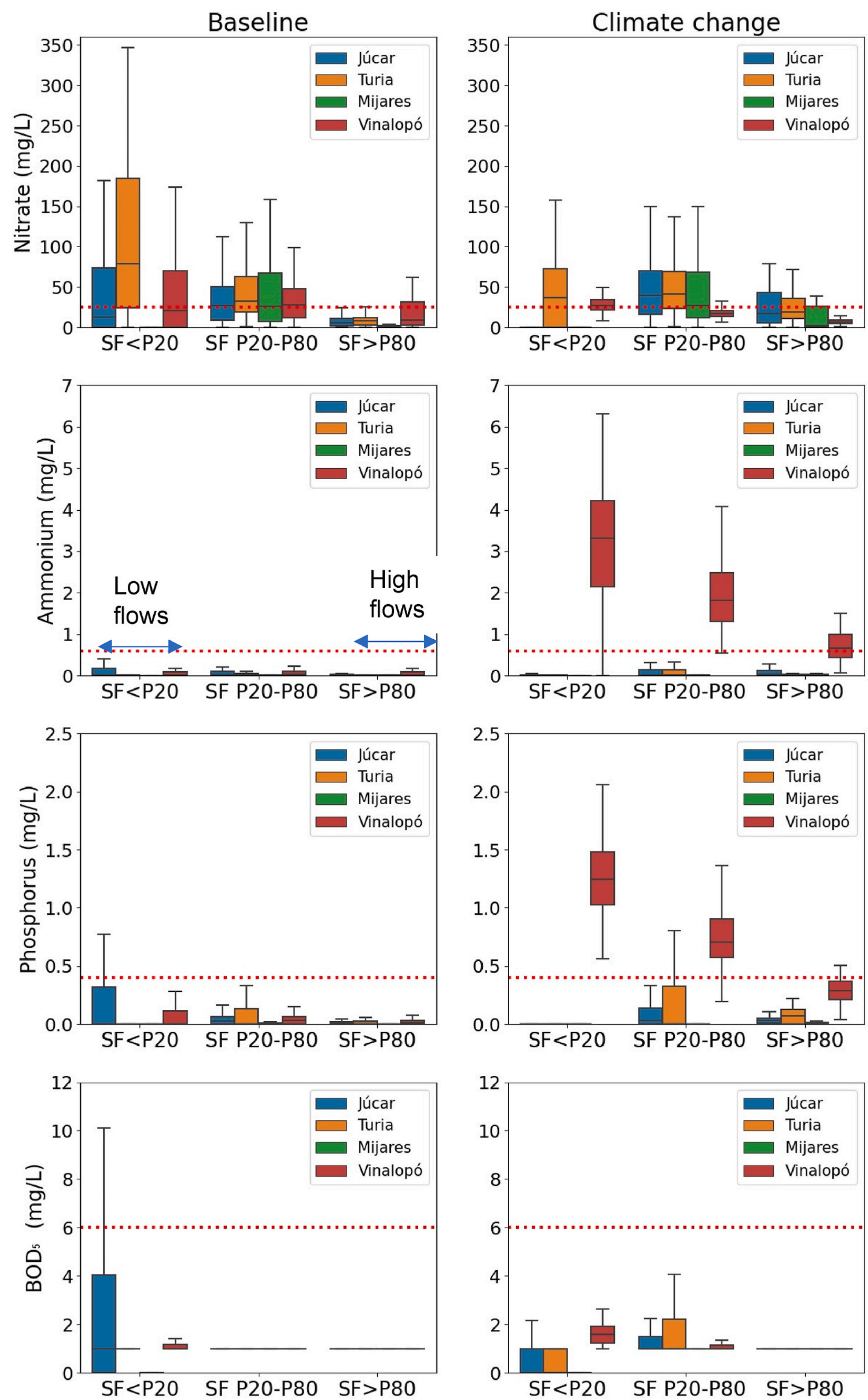

Fig. 9. Surface water concentration of nitrate, ammonium, phosphorus and BOD_5, by flow regimes (Low flow < P20, High flow > P80), using the threshold level method. The data correspond to tributaries of the Júcar, Turia and Mijares rivers and the main axis of the Vinalopó river downstream. Dashed lines represent the threshold, bad/good status, for each variable according to Spanish regulation for SW.

point loads.

The ammonium status was affected in the scenarios of reduction of point load with a decrease of 13%, 40%, 87%, and 100% of water bodies in poor status, corresponding to PP75, PP50, PP25 and PP0, respectively (Fig. 8). Reducing the point load by 50% (PP50) would result in a similar number of water bodies in poor status in the baseline and in the far future. The SP25 scenario improved the number of water bodies in good ammonium status from 94% to 96%.

The number of water bodies in poor phosphorus status decreased 33%, 75%, 92%, and 100%, corresponding to the scenarios PP75, PP50, PP25 and PP0, respectively (Fig. 8). As for phosphorus, a similar situation as in the baseline was achieved by reducing the PP by half. BOD_5 status was affected in the scenarios of reduction of point load with a decrease of 50%, 75%, 75%, and 100% of water bodies in poor status, corresponding to PP75, PP50, PP25 and PP0, respectively (Fig. 8).

The status of ammonium, phosphorus and BOD_5 in SW would be in a similar situation to the baseline in the distant future, if the point loads of the WWTP were reduced to 50%. In the far future, decreasing the point loads of ammonium, phosphorus and BOD_5 to 25% would significantly improve the number of water bodies in good status. In contrast to the other nutrients and BOD_5, the nitrate status would not improve substantially with the reduction of point source pollution. Measures to reduce nitrate concentrations should be targeted at reducing DP. According to the results, in order to achieve a nitrate status in the far future similar to the baseline, it would be necessary to reduce the DP load by 25% (DP75).

3.4. Effect of streamflow on the nutrient and BOD_5 concentration

Nutrients and BOD_5 concentrations were grouped by low, standard and high flow (P20, P20-80, P80) using the threshold level method (Fig. 9). This assessment was only applied to the downstream tributaries of the Júcar, Turia and Mijares river basins, and the main course of the Vinalopó river, because these were the most affected areas with water bodies in poor status.

For nitrate in the baseline (Fig. 9), the median nitrate concentration of the low flow was close to the threshold in the tributaries of the Júcar, Mijares and Vinalopó rivers, while in the Turia river the median exceeded the threshold and very high concentrations were reached. With standard flow, the median concentration exceeded the threshold in all tributaries and in the river Vinalopó. When the flow was high, the concentration of nitrates decreased and high values were only found in Vinalopó. In general, in the baseline nitrate concentrations were higher during dry periods than in high flow periods. Under the far-future climate change scenario, nitrate concentrations at low flow could decrease, while standard conditions meant concentrations could further increase above the threshold. In addition, when high flow events occurred, values above the threshold might be reached.

Phosphorus and ammonium followed a similar pattern both in terms of the baseline and climate change (Fig. 9). The median concentration of these nutrients remained below the threshold in the baseline, while under climatic change the concentration increased strongly in the Vinalopó river with low and standard flows. At low flow the median ammonium and phosphorus concentration could be twice as high as when the flow rate was standard.

The concentrations of BOD_5 were not affected by changes in flow, the mean concentration in the lower catchments remained below the threshold under both baseline and climate change conditions. This was because the percentage of water bodies affected by BOD_5 failures was very low.

4. Discussion

As shown in previous sections, changes in concentrations of the far future nutrients and BOD_5 in the Júcar RBD would be expected due to changes in rainfall, and temperature. The change in projected nitrate concentration was relatively minor compared to the changes in phosphorus, ammonium, and BOD_5. However, nitrates remain one of the main pollution problems in the Júcar RBD, as the surface area affected remains the same and is expected to increase by a factor of 1.3 in the far future. These results were consistent with the findings of nitrate concentration and climate change studies in other basins (Whitehead et al., 2009; Martínková et al., 2011; Jin et al., 2012; Čerkasova et al., 2018). However, they contrasted with results from Mediterranean basins in Portugal and Spain, where a decrease in nitrate loading as a result of climate change was predicted by the end of the century under RCP8.5 (Serpa et al., 2017; Buonocore et al., 2021). The contrasting changes in nutrient loads were not unexpected, as nutrient sources can vary considerably between basins. Climate change simulations showed that, although phosphorus and BOD_5 are of little concern at the moment, the poor SW quality of these elements will increase fourfold in the far future. Similar results were obtained by (Zhang et al., 2020), who reported an increase in the phosphorus loading due to climate change.

Overall, the water bodies with the greatest environmental problems are tributaries or intermittent rivers in the Júcar RBD. This may be because for most of the simulated period the flow through the water body was equal to the WWTP effluent. Therefore, the dilution process did not take place and pollutant removal only occurred through self-purification. Dilution is one of the most important physical phenomena for reducing pollutant concentrations in aquatic ecosystems (Li et al., 2022; Pang et al., 2023; Wang et al., 2023). Temporary aquatic ecosystems are therefore particularly vulnerable to such cases.

According to the results, if 25% of diffuse nitrate pollution, and 50% of point loads of ammonium, phosphorus, and BOD_5, are reduced, the current status of water bodies would be maintained in the far future, avoiding the effects of variations in temperature and rainfall (Fig. 8). This is in line with the EU's "farm to fork" strategy (European Commission, 2020), which aims to ensure sustainable food production by reducing nutrient losses by at least 50%, and therefore reducing fertiliser use by at least 20% by 2030. (Barreiro-Hurle et al., 2021) simulated the effect of the "farm to fork" strategy and found a reduction in the gross nitrogen balance of 42% in the European Union. In response to the "farm to fork" strategy, the Spanish Government has established a guide for action in the field of water policy. The actions to minimise the effects of nitrates on water resources include establishing zones vulnerable to nitrate pollution, increasing water quality sampling stations, and coordinating technical and agricultural activities (MPR, Ministerio de la presidencia, 2022). Irrigation modernisation, including fertigation, is in perfect alignment with the European strategy. It has the potential to decrease nitrogen application in agriculture by 25%–45% and reduce excess nitrogen production by 70%–83% (Pérez-Martín and Benedito-Castillo, 2023).

However, maintaining the current conditions of nutrient status in rivers is not sufficient to achieve the objectives proposed in other regulations that seek to protect the environment. Nitrate pollution in the Júcar RBD is mainly due to DP, but there are other important elements, such as the interaction between the river and the aquifer, which must be taken into account in the action plans in this territory. Therefore, water quality measures should continue to focus on reducing nutrient loading. In addition, the value of water resources in good status is often underestimated, due to the omission of other types of benefits. (Gourevitch et al., 2021) reported that the total benefits of improved water quality might exceed the costs of reducing phosphorus loading.

In the baseline, nitrate concentrations are high with lower flows, which is probably because there is an important runoff from agriculture, and there are also some significant sewage discharges. Conversely, with climate change nitrate concentration at lower flows tending to decrease (Fig. 9), this may be because the flow velocity is reduced and temperatures are higher; therefore, large amounts of nitrate may be lost through the denitrification process. This result agrees with other studies that reported that under low flows the nitrate concentration can decrease because the efficiency of denitrification increases (Mosley, 2015; Mishra et al., 2021; Zhou et al., 2022). Simulation suggests that by the end of the century denitrification has a greater effect than lack of dilution on nitrate concentrations. This is in accordance with (Whitehead et al., 2009; Qiu et al., 2023), who reported changes in long-term nitrogen dynamics as a result of climate change.

In contrast to nitrates, with climate change phosphorus and ammonium concentrations are expected in the far future to decrease during high flows and to increase twofold during low flows. This is due to a decrease in dilution of discharges and agricultural runoff. Similar patterns of change over the year in phosphorus concentration were found by Whitehead et al. (2009), El-Khoury et al. (2015) and Charlton et al. (2018). Unlike the other river sections, the river Vinalopó has several points of discharge along its course, therefore, and with reduced flow the dilution potential becomes less, which could greatly increase solute concentrations in the far future.

Future patterns of nutrient loads will be determined not only by environmental change, but also by nutrient sources. According to (Mehdi et al., 2015), climate change simulations combined with crop land use change scenarios showed non-linear dynamics in which the direction and scale of impacts were not predictable from the single changes alone. (Tong et al., 2012) found that climate change combined with land use changes increased nitrogen concentration compared to climate change alone. For future studies in the Júcar RBD, it is recommended to include land use scenarios and to build these scenarios with stakeholders in order to understand the reality of cropping systems and their management in the basin.

The results presented contain a number of inherent uncertainties. The uncertainties due to the application of climate simulations in a hydrological model are related to the climate change scenario, the regionalization technique, the choice of the hydrological model, the input data and the calibration process (Seidenfaden et al., 2022). In order to reduce this uncertainty, the study was carried out with the rainfall and temperature variations of a regionalised model. The regionalised model was a coupling of several models, and the hydrological models were calibrated with several flow and water quality stations.

Within the Júcar RBD, it is imperative to contemplate pollution reduction alternatives prior to discharging wastewater into water bodies. This is especially critical due to the intermittent nature of numerous watercourses in the region, where the circulating water originates from wastewater treatment plants or arises from diffuse pollution caused by agriculture. Strategies to mitigate the impact of discharges from WWTP include wastewater treatment technology, infrastructure upgrades, sustainable practices for resources and waste management, among others (Illueca-Muñoz et al., 2008; Crini and Lichtfouse, 2019; Kim et al., 2022; Sathya et al., 2023). Innovations such as membrane and biological nutrient removal systems offer higher removal efficiencies for pollutants, ranging from suspended solids to nitrogen and phosphorus compounds (Shehata et al., 2023). Membrane biological reactors have shown superior performance to traditional activated sludge processes in WWTP, their large surface area and high biomass concentration resulting in efficient adsorption and biodegradation capacity (Li and Zhang, 2018). Infrastructure upgrades, particularly phosphorus stripping techniques enhance the potential for P recovery (Gonzalez-Silva et al., 2022). Also, the use of chemical precipitation and biological phosphorus removal methods in WWTP ensures that excess phosphorus is reduced before wastewater enters water bodies (Crini and Lichtfouse, 2019).

Recently, sustainable water practices such as the reductions in water use, reuse of treated wastewater for non-potable uses and the integration of stormwater management approaches have effectively reduced the volume of wastewater discharge (Smol et al., 2020). Reclaimed water has great potential to be used for irrigation and other non-potable uses, which would reduce the high-water pressures caused by agriculture. It should be emphasised that wastewater can also be used to recover other resources such as nutrients, cellulose, biopolymers and fertilisers, thereby increasing the profitability and sustainability of the process (Foglia et al., 2023).

The adoption of nature-based solutions can be an appropriate and sustainable method to address excess nutrient pollution (Liquete et al., 2016; Liu et al., 2023). Higher nutrient removal efficiency is anticipated for nature-based solutions methods that address concentrated pollution, such as constructed wetlands and buffer strips in surface waters, compared to those addressing diluted pollution, like vegetated drainage ditches (Mancuso et al., 2021; Rizzo et al., 2023). Regarding buffer strips, the literature reports a median removal rate of approximately 72% for total nitrogen and 74% for total phosphorus. Additionally, in terms of area load, the median for attached pollutants is 26.9 mg/L for total nitrogen and 4.4 mg/L for total phosphorus (Rizzo et al., 2023).

According to a review by Nan et al. (2020) on constructed wetland-based water treatment systems, the integration of constructed wetlands with additional technologies such as ultraviolet treatment and anaerobic reactors can enhance their performance, resulting in superior removal efficiencies compared to conventional horizontal and vertical subsurface flow constructed wetlands. Ramprasad et al. (2017), based on a horizontal subsurface flow constructed wetland in a green rooftop water recycling system, reported remarkably high overall removal rates for tested nutrients: BOD (90.8%), total nitrogen (91.7%), and total phosphorus (87.9%).

In Spain, research pertaining to the performance of a horizontally subsurface flow constructed wetland in treating artificially aerated domestic wastewater indicated that the enhanced system demonstrated effectiveness in removing total nitrogen (91.5%), total phosphorus (96.9%), total suspended solids (97.5%), and BOD_5 (97.8%) (Andreo-Martínez et al., 2017). The authors concluded that improved single-stage constructed wetlands can elevate contaminant removal and meet standards for reclaimed wastewater reuse in agriculture. Similarly, constructed wetlands are suitable technologies for agricultural wastewater from diffuse sources, which typically exhibit varying pollutant concentrations compared to point source wastewater.

5. Conclusions

This study assessed the projected change in water quality status under long-term climate change-induced increases in temperature and rainfall with a constant diffuse and point source pollution load over time in the Júcar RBD. According to the results found in this study, climatic conditions would change the polluting effect of the current nutrient loads going into the water bodies. The water bodies of the Júcar RBD were mainly affected by nitrate pollution, and in the far future the affected area would be expected to increase by a factor of 1.3. However, the water bodies in poor status due to ammonium, phosphorus and BOD_5 would increase by factors of 1.9, 4, and 4, respectively. One of the main problems that the district could face in the future would be the lack of dilution of pollutant loads when low flows occur, as loads could increase up to twofold and most of the affected water bodies are tributaries or intermittent rivers. Strategies to improve the status of water bodies for nitrate concentrations should focus on reducing diffuse pollution, specifically in irrigated agricultural areas. On the contrary, in order to improve the status for phosphorus, ammonium and BOD_5, actions should focus on reducing point loads close to large towns and cities. Reducing 25% of diffuse nitrate pollution and 50% of point loads of ammonium, phosphorus and BOD_5 would maintain the current status of water bodies in the far future, avoiding the effects of temperature and rainfall variations. However, these reductions in point and diffuse loads would not be sufficient to meet the environmental objectives imposed by the EU. Effective pollution reduction strategies should involve a combination of efforts, including improved wastewater treatment technologies, sustainable agricultural practices and the adoption of nature-based solutions. Collaboration between stakeholders is essential for successful implementation. Nature-based solutions, such as constructed wetlands and buffer strips, offer promising ways to remove nutrients and improve water quality. In future studies in the Júcar RBD, it is recommended that changes in agricultural systems are considered alongside different land uses; these scenarios should be built with stakeholders to understand the reality of the basin.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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