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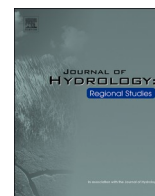
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Ecohydrologic modeling using nitrate, ammonium, phosphorus, and macroinvertebrates as aquatic ecosystem health indicators of Albaida Valley (Spain)

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ABSTRACT

Study region: Albaida Valley, Spain.

Study focus: Rivers are experiencing a rapid biodiversity loss largely due to water quality degradation imposed by anthropogenic activities. To show the capability of modeling to inform water management at watershed scales, this research develops an eco-hydrological model of the Albaida Valley (Spain). SWAT (Soil and Water Assessment Tool) is used for modeling of discharge and nutrients after calibration with SWAT-CUP (SWAT Calibration and Uncertainty Program). Results from SWAT are coupled to regressions between nutrients concentrations and macroinvertebrate-based metrics obtained from field monitoring. The spatio-temporal assessment of ecological status of streams is then carried out using simulated chemical and biological quality indicators (nitrate, ammonium, phosphorus, and macroinvertebrates).

New hydrological insights for the region: Management measures (e.g., improving treatment of wastewater and/or adopting policies for reducing fertilizer use) are needed as the ecological status of Albaida Valley rivers is mostly classified as poor because of nutrients pollution. The reasonably low uncertainty in the model prediction (expressed by R-factor: discharge (0.2–0.61), nitrate (0.79–1.27) and total phosphorus (0.8–1.68)) demonstrates the potential of the presented model for future applications (i.e., for investigating possible responses of the Albaida Valley ecosystem to changes in climate, land-use, and local management policies). The modeling approach provided in this study could be generally used as a complementary technique to field monitoring in assessing and managing ecological conditions of rivers.

1. Introduction

Anthropogenic degradation of freshwater ecosystems is undermining their ability to provide benefits to humans and other species (Naiman and Turner, 2000; Carpenter et al., 2011). Excessive water withdrawal, urbanization, agriculture, deforestation, and global

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warming are important stressors that severely damage freshwater environments (Jackson et al., 2001; Carone et al., 2009; Luo et al., 2018; Wilkinson et al., 2018; Pham et al., 2019; Lin et al., 2021). However, nutrient pollution is indeed a major contributor to river degradation (EEA, 2018; Carvalho et al., 2019). While agricultural and urban land uses are associated to important diffuse sources of nutrients, effluents of WWTPs can also significantly contribute to nutrient loads in downstream reaches, despite the extensive treatment of wastewater prior to discharge in receiving waters. The impact of effluents from WWTPs could be even more prominent during dry periods in semi-arid and arid areas, since most of the flow in the river channel is mainly composed of WWTP effluent (Dennehy et al., 1998; Passell et al., 2005; Carey and Migliaccio, 2009; Maier et al., 2009; López-Doval et al., 2013; Ladapo and Aminu, 2017; Preisner et al., 2020).

Recognizing the importance of freshwater conservation, several programs and agreements such as the European Water Framework Directive, the U.S. Clean Water Act, the Minamata Convention, the International Commission for the Protection of the Rhine, and the Chinese Grain for Green Program have been developed to protect river biodiversity and ecosystem functioning. However, more efforts are still required to implement such policies, as many water bodies have not reached the acceptable water quality standards yet. In Europe, for instance, around 60 % of surface water bodies failed to achieve the good ecological status in 2018 and it is predicted that achieving the desired objectives of the WFD by 2027 would be a challenge in many countries (European Commission, 2019; Dedić et al., 2020).

Watershed modeling can assist scientists and policymakers to determine and develop comprehensive management strategies and policies, and to measure the effectiveness of existing programs (Moriassi et al., 2007; Oliver et al., 2016). Many studies nowadays benefit from computer models to simulate hydrology, water quality, and different complex processes in watersheds (Girbaciau et al., 2015; Suryavanshi et al., 2017; Jeong et al., 2020; Maleki Tirabadi et al., 2021). Using different simulators and tools, the impacts of point source and nonpoint source pollution on water quality (Wu and Chen, 2013; Li et al., 2017), the eutrophication of water bodies (Jin et al., 1998; Wang et al., 1999; Wool et al., 2003; Dabrowski, 2014), and the possible impacts of climate or/and land use changes on quantity or/and quality of water resources in different continents such as Africa (Githui et al., 2009); Asia (Narsimlu et al., 2013; Park et al., 2013; Boongaling et al., 2018; Chotpantarat and Boonkaewwan, 2018; Ganji and Nasser, 2021), North America (Ye and Grimm, 2013; Ahmadi et al., 2014; Gombault et al., 2015; Alam et al., 2018), and Europe (Bouraoui et al., 2002, 2004; Varanou et al., 2002; Boorman, 2003; Pinaras et al., 2010; Marcinkowski et al., 2017; Szalińska et al., 2021) have been evaluated. For instance, a study conducted in Central Spain (Molina-Navarro et al., 2014) indicates that climate and land use changes could noticeably impact both water availability and quality in the Pareja Limno-reservoir. Dabrowski (2014) discussed that poor sewage treatments have the potential to considerably change the trophic status of reservoirs. In another study, Chotpantarat and Boonkaewwan (2018) found that nitrate and phosphate loads along the Lower Yom River in Thailand increase because of the spread of agriculture and urbanization. In addition, studies demonstrated that anthropogenic pressures are strongly associated with the degradation of fluvial habitat leading to significant alterations in aquatic communities (Martínez Mas et al., 2004; Al-Shami et al., 2011; Dahm et al., 2013; Jiménez and Pérez, 2013; Martínez, 2013; Marzin et al., 2013; Berger et al., 2017; Menció and Boix, 2018). Focusing on selected fish and macroinvertebrates species, Guse et al. (2015) predicted that the habitat suitability in the Treene River, Germany, will be influenced by changes in climate and land use. In another study, Schmalz et al. (2015) suggested that the species richness would be affected by deforestation in the Changjiang River Watershed, China. The results of a study conducted in Turkey indicate that the richness and composition of macroinvertebrates in the Kucuk Menderes River vary as the river becomes polluted by flowing through residential, industrial, and agricultural areas (Arslan et al., 2016). Mesgaran Karimi et al. (2016) also showed that the effluents of two trout farms have significantly decreased the diversity of macroinvertebrates in the Dohezar Stream, Iran.

River ecological assessment has progressed significantly in the last few decades (Poikane et al., 2021). In Europe, the Water Framework Directive (WFD, 2000/60/EC) is the main legislation for achieving good ecological status, and the relationships between nutrients, biological structure, and ecological status in rivers are explored based on the concept behind the WFD (Kelly et al., 2009; Poikane et al., 2020). Most of the studies conducted on river biodiversity (e.g., Al-Shami et al., 2011; Arslan et al., 2016; Mesgaran Karimi et al., 2016; Menció and Boix, 2018) are based on datasets resulting from river sampling campaigns. In addition to the knowledge derived from these experimental studies, watershed-scale models have the capability to complement these studies by investigating the response of freshwater ecosystem to different environmental stressors at various places and times other than the sampled ones, and also to strengthen our understanding by predicting the ecosystem response to different stressor scenarios. Thus, the main objective of the present study is to evaluate the potential of an integrated modeling approach in predicting the water quality and the ecological response to different hydrological management scenarios. In particular, in the current work the SWAT (Soil and Water Assessment Tool) software is used to build an ecohydrological model of an agricultural catchment in Spain, and the evaluation of ecological conditions of stream network are evaluated by coupling outputs of the SWAT model and regressions between nutrients concentrations and macroinvertebrate-based metrics. The chosen approach allows to quantify model uncertainty, which has been discussed as a crucial step for watershed modeling (Abbaspour et al., 2015).

2. Materials and methods

An ecohydrological modeling approach is developed in the present study to evaluate ecological status of the Albaida Valley streams. For this purpose: (1) a variety of information is collected to characterize the case study; (2) the SWAT model (Arnold et al., 1998) is used to simulate discharge and nutrient loads after calibration with SWAT-CUP (SWAT Calibration and Uncertainty Program) (Abbaspour et al., 2007); (3) Concentrations of the major nutrients affecting water quality are simulated with the calibrated model; (4) regressions between nutrients concentrations and macroinvertebrate-based metrics built from an independent dataset are coupled to SWAT generated concentrations; and (5) the ecological response of streams to current water and wastewater management in the

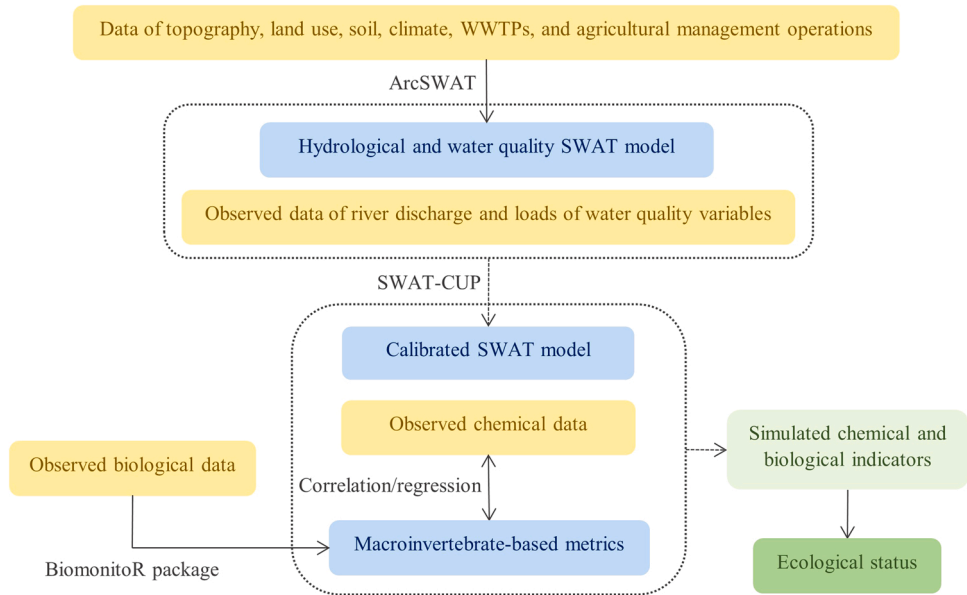


Fig. 1. Overview of the eco-hydrological modeling approach applied in this study.

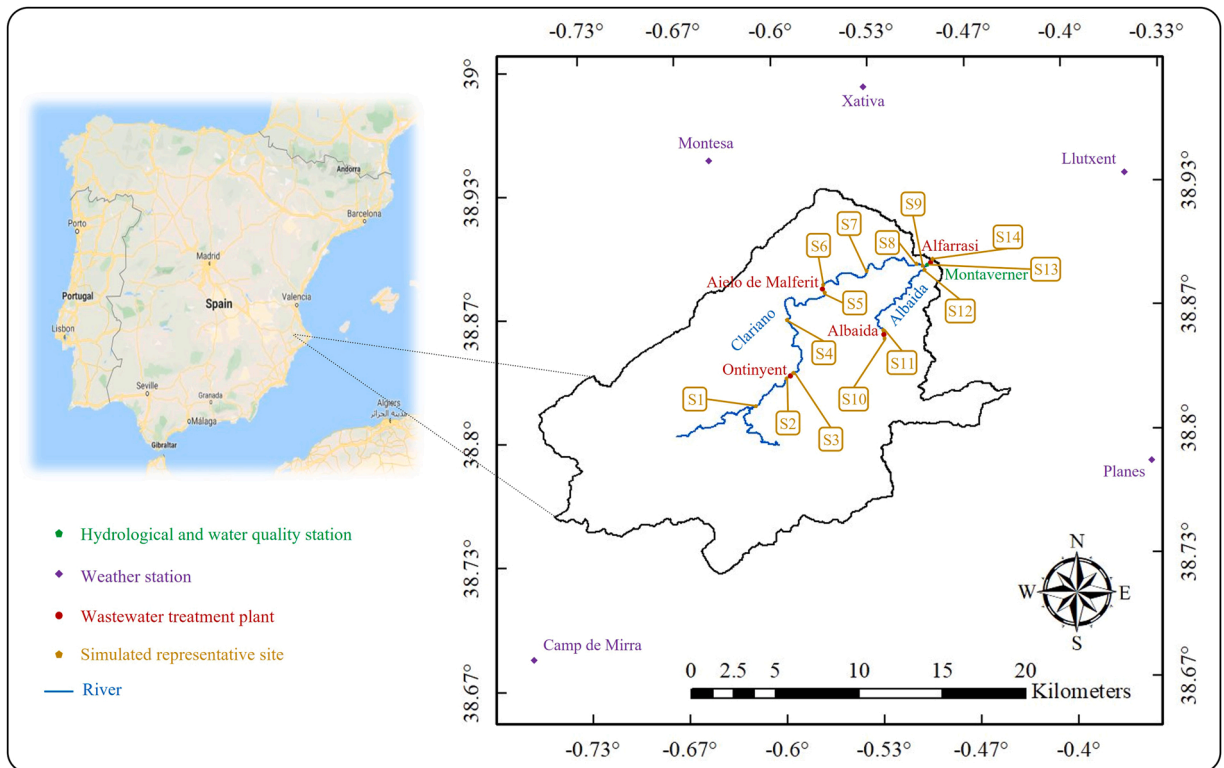


Fig. 2. Location of the study area, hydrological, water quality and meteorological stations, WWTPs, and representative sites simulated with SWAT.

Table 1
Overview of data used in the present study.

Data	Description	source
Topography	<ul style="list-style-type: none"> DTM25: Digital Terrain Model with 25 m grid spacing 	Spanish National Geographic Institute, (IGN, 2021)
Land use	<ul style="list-style-type: none"> MCA 2000–2010: the land use and crop map of Spain with a scale of 1:50,000 	Geographic Information System of Agricultural Data, the Ministry of Agriculture, Fisheries and Food of Spain, (SIGA, 2021)
Soil	<ul style="list-style-type: none"> HWSD v1.21: Harmonized World Soil Database version 1.21 with a resolution of about 1 km (a 30 arc-second raster database) 	(FAO/IIASA/ISRIC/ISSCAS/JRC, 2012)
Precipitation Minimum temperature Maximum temperature Solar radiation Relative humidity	<ul style="list-style-type: none"> Daily data Period: 2002–2017 Five stations: Planes, Llutxent, Xativa, Montesa, and Camp de Mirra 	Valencian Institute for Agricultural Research, (IVIA, 2021)
Wind speed	<ul style="list-style-type: none"> Daily data Period: 2002–2017 Four stations: Planes, Xativa, Montesa, and Camp de Mirra 	Valencian Institute for Agricultural Research, (IVIA, 2021)
River discharge	<ul style="list-style-type: none"> Daily data Period: 2005–2017 Montaverner Station 	The Water Information System of the Júcar Hydrographic Confederation, (Júcar, 2021)
River suspended solids/ nitrate/phosphorus loads	<ul style="list-style-type: none"> Monthly to trimonthly data Period: 2005–2017 Montaverner Station 	The Water Information System of the Júcar Hydrographic Confederation, (Júcar, 2021)
WWTP	<ul style="list-style-type: none"> Data include: the effluent flow rate, suspended solid, CBOD, mineral phosphorus, nitrate, ammonia, organic phosphorus. Monthly data Period: 2002–2017 Four WWTPs: Aiello de Malferit, Albaida, Alfarrasi, and Ontinyent 	The Public Entity for Sanitation of Wastewater, Valencia, Spain, (EPSAR, 2021)
Agricultural management operations	<ul style="list-style-type: none"> Planting, harvesting, fertilization and irrigation 	(DOGV, 2000; Ramos et al., 2002; Cantero-Martínez et al., 2003; De Paz and Ramos, 2004; Romero et al., 2006; Morell et al., 2011; FAO, 2021)
Chemical/biological data, Albaida Valley	<ul style="list-style-type: none"> Chemical data include: the concentrations of nitrate, nitrite, ammonium, phosphate, and total phosphorus Biological data include: the abundance of macroinvertebrates at family level Six sampling sites Sampling period: 2010–2012 	The Ecological Coordinator of the Albaida Valley (CEVA) and Universitat Politècnica de València, (Jiménez and Pérez, 2013; Martínez, 2013)
Chemical/biological data, Catalonia Region	<ul style="list-style-type: none"> Chemical data include: the concentrations of nitrate, nitrite, ammonium, and phosphate Biological data include: the abundance of macroinvertebrates at family level 117 sampling sites Sampling period: 2015–2020 	The Catalan Water Agency, (ACA, 2021)

Albaida Valley is evaluated using simulated chemical and biological indicators. Fig. 1 shows the overall methodology applied in the study.

2.1. Study area

The Albaida Valley (Valencia Province, Eastern Iberian Peninsula) is a well-defined southwest-northeast syncline valley surrounded by the Serra Grossa and the Agullent-Benicadell Mountains reaching up to around 1100 m (García Atiénzar, 2007). In the present work, a shrubland and agricultural dominated part of the valley with an approximate area of 320 km² is studied (Fig. 2). The region is characterized by a semi-arid Mediterranean climate with mean annual temperature between 13 °C and 17 °C (depending on the specific location), mean annual precipitation between 400 mm and 800 mm, and mean annual evapotranspiration between 700 mm and 900 mm, and the summer drought period is also from June to August (SIGA, 2021). The valley consists of the Clariano and Albaida River Watersheds. The Albaida River, that is a tributary of the Júcar River, originates from Benicadell Mountain, and the Clariano River forming in Bocairent is its main tributary with a length of 37 km. The behavior of the Albaida River differs at upstream and

downstream of the confluence with the Clariano River as it receives important contributions from the Clariano River that is severely affected by the effluents of WWTPs. A few kilometers downstream of their confluence, the Albaida River flows into the Bellús Reservoir which is one of the most polluted reservoirs in the Valencian Community. In fact, high values of nutrients compounds from point and nonpoint sources have led to water quality degradation and the loss of biodiversity in the rivers and the reservoir (García Atiénzar, 2007; CHJ, 2019).

2.2. Data description

As further discussed below, a diversity of information is used in this work to describe the study area (Table 1), including a Digital Terrain Model (IGN, 2021), a land use and crop map of Spain (SIGA, 2021), the Harmonized World Soil Database (HWSD) version 1.21 (FAO/IIASA/ISRIC/ISSCAS/JRC, 2012), meteorological data of precipitation, temperature, solar radiation, wind speed and relative humidity, hydrological and water quality data, flow rate and concentration data of four WWTPs (EPSAR, 2021), chemical and biological observations of rivers resulting from different research projects and monitoring and control programs (Jiménez and Pérez, 2013; Martínez, 2013; ACA, 2021), and information about agricultural management operations (DOGV, 2000; Ramos et al., 2002; Cantero-Martínez et al., 2003; De Paz and Ramos, 2004; Romero et al., 2006; Morell et al., 2011; FAO, 2021). According to the DTM25 (IGN, 2021), the mean slope of the area is about 18.3 % and the mean elevation is approximately 499.3 m. The land use and crop map of Spain, MCA 2000–2010 (SIGA, 2021), also represents that the area is dominated by agricultural landscape (47.2 %, cultivated with orchards, olive groves, vineyards, and several herbaceous crops) and shrubland (30.4 %). The rest of the area is covered by forest (16 %), urban areas (5.4 %), and water (1 %). According to HWSD v1.21 (FAO/IIASA/ISRIC/ISSCAS/JRC, 2012), loam and clay are the prevailing soil textures of the area, and the hydrologic soil groups are B and D.

2.3. The SWAT model setup

SWAT is a physical-based, semi-distributed watershed-scale simulation model developed by the United States Department of Agriculture that operates on a daily time step. SWAT has been widely applied in hydrologic and water quality studies around the globe (Anand et al., 2018; Gong et al., 2019; Wang et al., 2020) as it has a user-friendly graphical interface and GIS link and enables long-term environmental impact assessments. In SWAT, a watershed is partitioned into a number of sub-watersheds which are further subdivided into areas called Hydrologic Response Units (HRUs) containing unique soil, land use, and slope attributes (Neitsch et al., 2011; Arnold et al., 2012, 2013; Shin et al., 2019). The ArcSWAT 2012, an ArcGIS extension and interface for SWAT, is used in this study to simulate water quantity and quality of streams in the Albaida Valley. In the first step, the 25-m resolution DTM (IGN, 2021) is used to delineate the study area, and 14 representative sites (see Fig. 2) are also defined for farther analyses of changes in ecological status along the Clariano and Albaida Rivers. Land-use (MCA 2000–2010) (SIGA, 2021) and soil data (HWSD v1.21) (FAO/IIASA/ISRIC/ISSCAS/JRC, 2012) are then added, and slope classes are defined. Fig. S1 and table S1 in the Supplement present the distribution of land-cover, soils, and slope. Based on land-use, soil, and topography information, the study area is divided into 16 sub-watersheds and 844 HRUs. In the following step, data of daily precipitation, minimum and maximum air temperature, solar radiation, wind speed and relative humidity of five stations (Planes, Llutxent, Xativa, Montesa, and Camp de Mirra; see Fig. 2) (IVIA, 2021) are entered into the model. As WWTP effluents affect the hydrology and water quality of the rivers, the effluent flow rates, and water quality data of four WWTPs (Aielo de Malferit, Albaida, Alfarrasi, and Ontinyent; see Fig. 2) (EPSAR, 2021) are also included in the model. In addition, several agricultural management operations such as planting, harvesting, fertilization and irrigation (as detailed in the Supplement, table S2) are applied to the model (DOGV, 2000; Ramos et al., 2002; Cantero-Martínez et al., 2003; De Paz and Ramos, 2004; Romero et al., 2006; Morell et al., 2011; FAO, 2021). In the present study, the SCS curve number procedure is used to calculate surface runoff, and the Penman-Monteith method estimates potential evapotranspiration (Monteith, 1965; SCS, 1972; Allen, 1986; Allen et al., 1989; Neitsch et al., 2011). Water and sediment are also routed through the channel network using the variable storage routing method and the simplified Bagnold equation, respectively (Williams, 1969; Bagnold, 1977; Neitsch et al., 2011). Based on available data, daily simulations are performed from 2002 to 2017. The first three years (2002–2004) are used for warming up the model and are excluded from analyses. The rest of simulations (2005–2017) are used for model calibration and validation.

2.4. The SWAT model calibration and uncertainty

The semi-automated SUFI-2 algorithm in the SWAT-CUP tool is used for calibration and uncertainty analysis as well as sensitivity analysis and validation (Abbaspour et al., 2018). In SUFI-2, the propagation of the uncertainty in parameters (through applying ranges) leads to the model prediction uncertainty which is quantified by the 95 % prediction uncertainty (the 95PPU). In fact, the 95PPU is the model output which is calculated from the 2.5 % and 97.5 % quantiles of cumulative distribution of output variables generated through Latin hypercube sampling (Abbaspour, 2015). To quantify the fit between simulation results (the 95PPU) and observed data, values of P-factor (the percentage of observed data enveloped by the 95PPU) and R-factor (the thickness of the 95PPU envelope quantifying the degree of uncertainty in the model prediction) are used (Abbaspour et al., 2007, 2015). A P-factor value of larger than 0.7 and a R-factor value of less than 1.2 would be acceptable for discharge modeling, while P-factor values of larger than 0.55, 0.45, and 0.4 and R-factor values of less than 1.8, 2.4, and 2.8 are recommended for simulating nitrate, suspended solids, and phosphorus, respectively (Abbaspour, 2020).

In the present study, the data of Montaverner Station (Fig. 2) including river discharge and loads of suspended solids, nitrate, and total phosphorus (Júcar, 2021) are used for model calibration and validation. A 7-year period (2005–2011) and a 6-year period

Table 2

Pearson's correlation coefficients between mean values of concentrations of nutrients and macroinvertebrate-based metrics analyzed at six sampling sites (S1, S3, S4, S7, S8, and S14)*.

Metric	PO ₄ ³⁻ (mg P/l)	NH ₄ ⁺ (mg N/l)	NO ₃ ⁻ (mg N/l)	NO ₂ ⁻ (mg N/l)	TP (mg P/l)
IBMWP	-0.82***	-0.38	-0.95**	-0.69	-0.80
NFAM	-0.74	-0.34	-0.93**	-0.73	-0.75
EPT	-0.71	-0.15	-0.97**	-0.52	-0.64
ASPT	-0.88***	-0.34	-0.95**	-0.65	-0.81

(*) Number of chemical samplings: 8 for S1, S3, S4, S7, and S8, and 13 for S14; number of biological samplings: 6 for S1, S3, S4, S7, and S8, and 11 for S14, (**) $P < 0.01$, (***) $0.01 < P < 0.05$

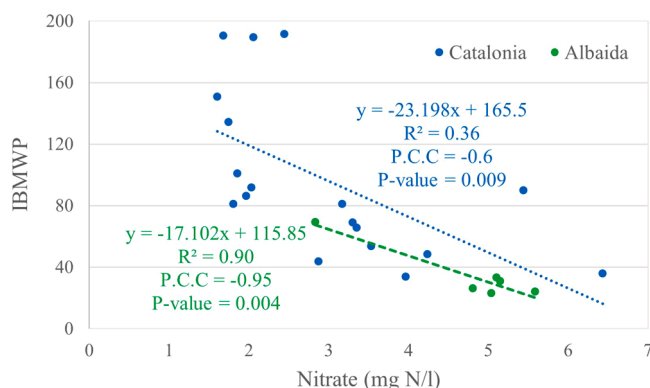


Fig. 3. Nitrate and IBMWP relationship in the Albaida Valley Region.

(2012–2017) are considered as calibration and validation periods, respectively. River discharge has been measured continuously, while the loads of suspended solids, nitrate, and total phosphorus have been measured irregularly (monthly to trimonthly) during these periods. Although suspended solid is not considered as an indicator of water quality in this study, we calibrate it because its calibration will help us in calibrating total phosphorus as phosphorus moves with sediments in the river. 500-simulation iterations are applied to calibrate the model. [Table S3](#) in the Supplement provides an overview of SWAT parameters calibrated in this study.

2.5. Chemical indicators

Nitrate, ammonium, and phosphorus are used in the present study as chemical water quality indicators of the Albaida Valley. Time series of concentrations of these nutrients are first generated based on time series of discharge and nutrients loads simulated with the SWAT model. Afterwards, generated concentrations are classified in different quality classes ([Table S4](#) in the Supplement) according to national directive of Spain ([Royal Decree 817, 2015](#)).

2.6. Biological indicators

This work focuses on macroinvertebrates as biological indicators of stream health. Macroinvertebrates represent the most important biological indicators in freshwater biomonitoring, due to their different sensitivity to changes in both water chemistry and habitat ([Bo et al., 2017](#)). Macroinvertebrate-based metrics are widely used to detect clean or polluted water as they can provide useful information of local conditions ([Camargo et al., 2004](#); [Clews and Ormerod, 2009](#); [Gombeer et al., 2011](#); [Nicacio and Juen, 2015](#)). Several macroinvertebrate-based metrics including IBMWP (Iberian Biological Monitoring Working Party), ASPT (Average Score Per Taxon), EPT (Ephemeroptera, Plecoptera, Tricoptera), and NFAM (Number of FAMilies) are used in the present study according to national directive of Spain ([Royal Decree 817, 2015](#)). These metrics are calculated from the abundance of macroinvertebrate families measured at six sampling sites (S1, S3, S4, S7, S8, and S14; see [Fig. 2](#)) ([Jiménez and Pérez, 2013](#); [Martínez, 2013](#)) by using the biomonitoR package (<https://github.com/alexology/biomonitoR/tree/main/R>). As macroinvertebrates communities may be influenced by extreme events (e.g., heavy rains), the river flow rate in the six months before the samples collection was checked, and no extreme events were found that may have affected these measurements.

In this study, Pearson's correlation analysis is first used to evaluate possible relationships between observed concentrations of nutrients and obtained macroinvertebrate-based metrics ([Table 2](#)).

As [Table 2](#) shows, all macroinvertebrate-based metrics are negatively correlated with nutrients concentrations, but correlations with nitrate are stronger and more statistically significant. Thus, nitrate is chosen as the best predictor for further analyses. In addition, IBMWP is selected among macroinvertebrate-based metrics (although all metrics are strongly correlated with nitrate) because BMWP is commonly used as biological quality metric ([Vitecek et al., 2021](#)), and recommended reference values of IBMWP are also available

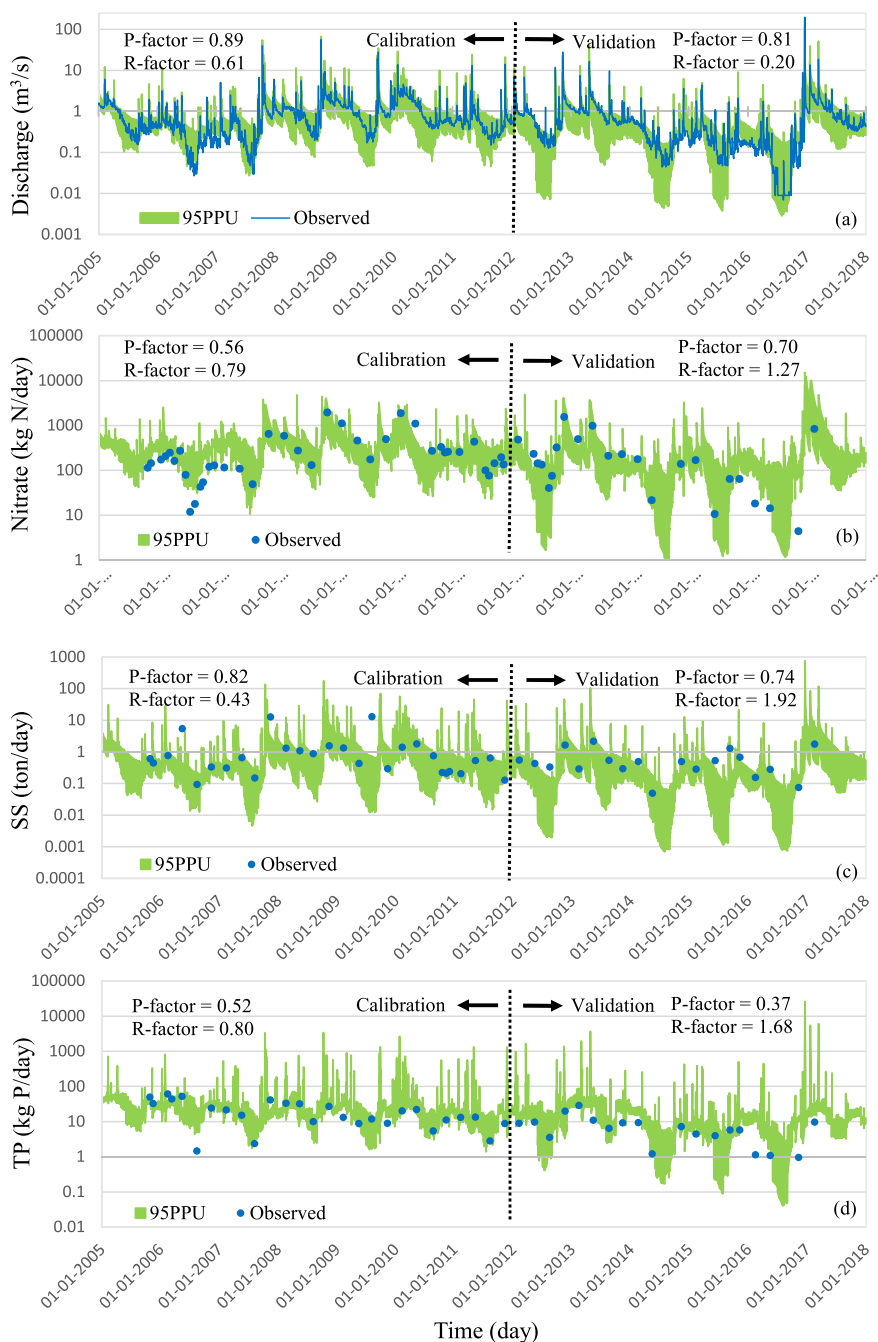


Fig. 4. Simulated and observed discharge (a), nitrate loads (b), suspended solids loads (c), and total phosphorus loads (d) at Montaverner Station. The difference between the lower and the upper bounds of the 95PPU demonstrates the necessity of quantifying and reporting the degree of uncertainty.

for different types of rivers of Spain (Royal Decree 817, 2015). In the next step, the regression equation is obtained from the linear regression analysis between observed concentrations of nitrate and observed values of IBMWP (Fig. 3). Because of the low number of sites in the Albaida Valley, data of 117 sampling sites within the Catalonia Region (table S5) (ACA, 2021) are also analyzed to verify the obtained regression equation from the Albaida Valley database shown in Fig. 3. These sampling sites have the same ecological characteristics of Clariano and Albaida Rivers (i.e., eco-type 9: low Mediterranean mountain mineralized rivers). Moreover, anthropic pressures for each sampling site are also specified (IMPRESS, 2020), and Cluster analysis (Legendre and Legendre, 1998) is then used to determine the sites that are similar to those in the study area (i.e., Albaida Valley) in terms of pressures. Finally, regression equations obtained from the data of selected sampling sites (i.e., 18 sites with the same ecological characteristics and pressures of the Albaida

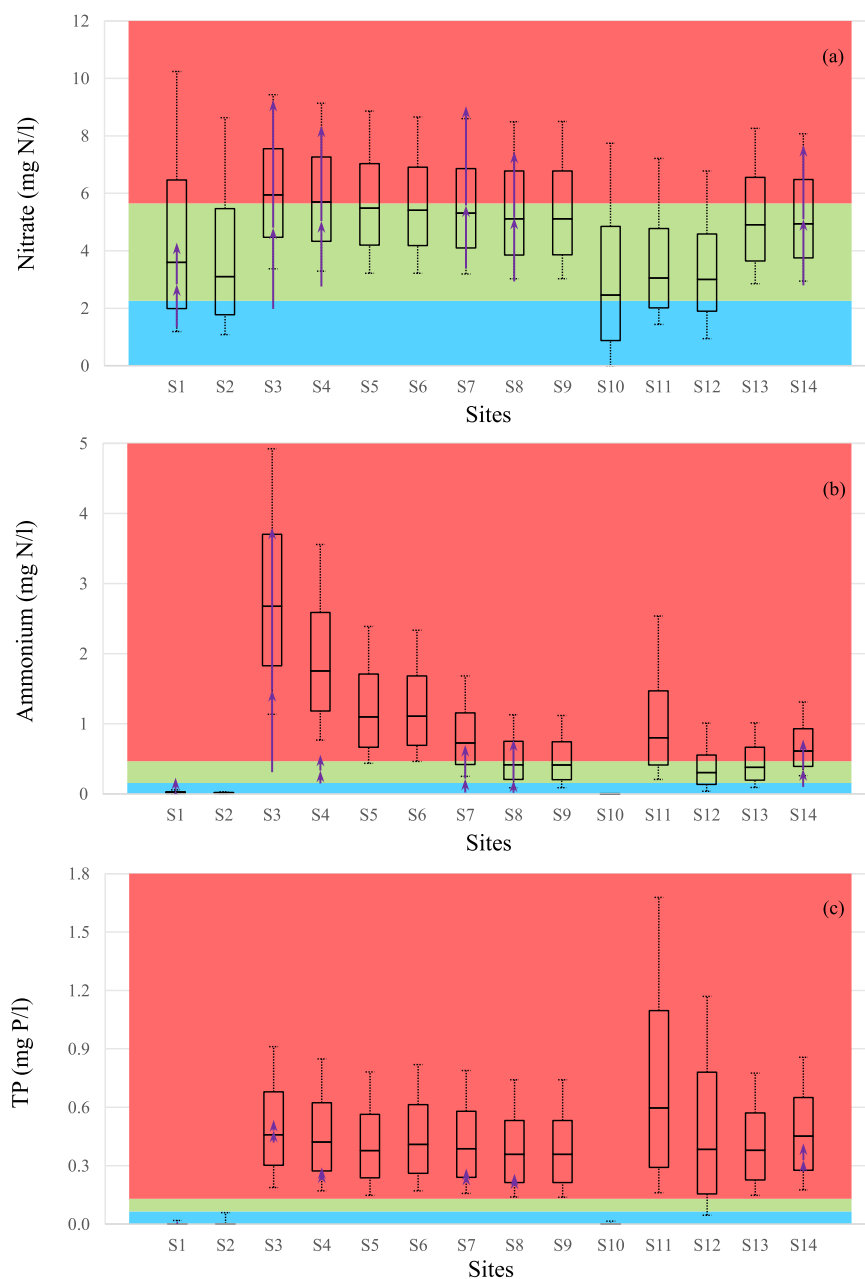


Fig. 5. Predicted chemical indicators of water quality of the Albaida Valley (expressed by concentrations of nitrate (a), ammonium (b), and total phosphorus (c)). Blue, green, and red areas represent high, good, and bad quality classes, respectively, according to [Royal Decree 817 \(2015\)](#). The reported box plots reflect both the temporal variability and the model prediction uncertainty. The box plot for each site results from SWAT-CUP outputs for the years 2005–2017 (i.e., based on 500×4748 concentration values simulated for each site where 500 is the number of simulations in SWAT-CUP and 4748 is the number of days during 2005–2017). The figure also reports the predicted concentrations of ammonium, although the model has not been calibrated for ammonium. The purple arrows show the range of observed concentrations at six sampling sites.

Valley) are compared with the ones resulted from the Albaida Valley database ([Fig. 3](#)). The results from Catalonia database support the reliability of the regression equation obtained from the Albaida database, because nitrate concentrations and IBMWP values are negatively correlated in both regions and the slopes of the equations for the two databases are also comparable (differences in intercept values can be explained by different degrees of pressures in each river), which indicates that the sensitivity of IBMWP values to changes in nitrate concentration is similar for rivers in the Catalonia and for the Albaida Valley rivers. The regression equation obtained from the Albaida database is hence used for the rest of the analysis: this equation is coupled to nitrate concentrations generated with the SWAT model to produce time series of IBMWP values. Produced values of IBMWP are finally classified in different quality classes ([Table S6](#) in the Supplement) according to national directive of Spain ([Royal Decree 817, 2015](#)).

Table 3
Chemical indicators status based on mean values of simulated concentrations of nutrients.

Site	Nitrate status	Ammonium status	Total Phosphorus status	Chemical indicators status
1	Good	High	High	Good
2	Good	High	High	Good
3	Bad	Bad	Bad	Bad
4	Bad	Bad	Bad	Bad
5	Bad	Bad	Bad	Bad
6	Bad	Bad	Bad	Bad
7	Good	Bad	Bad	Bad
8	Good	Bad	Bad	Bad
9	Good	Bad	Bad	Bad
10	Good	High	High	Good
11	Good	Bad	Bad	Bad
12	Good	Good	Bad	Bad
13	Good	Bad	Bad	Bad
14	Good	Bad	Bad	Bad

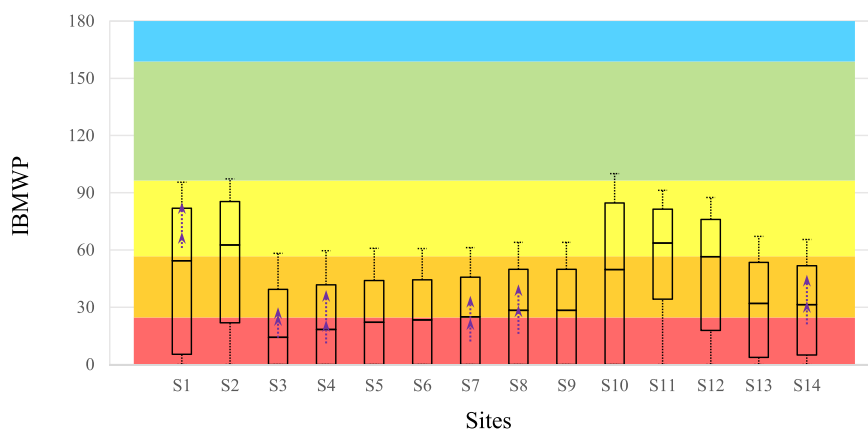


Fig. 6. Predicted values of IBMWP used as biological indicator of water quality of the Albaida Valley. Blue, green, yellow, orange, and red areas represent high, good, moderate, poor, and bad biological quality, respectively, according to [Royal Decree 817 \(2015\)](#). The reported box plots reflect both temporal variability and the model prediction uncertainty. The box plot for each site results from the coupling of the regression equation with nitrate concentrations estimated with SWAT-CUP for the years 2005–2017 (i.e., based on 500×4748 IBMWP values obtained for each site where 500 is the number of simulations in SWAT-CUP and 4748 is the number of days during 2005–2017). The purple arrows show the range of observed values of IBMWP at six sampling sites.

2.7. Ecological status

In the present study, the ecological status of the Albaida Valley rivers is evaluated by combining chemical and biological indicators. Based on predicted chemical and biological quality classes, streams of the Albaida Valley are classified into five ecological status classes ([Table S7](#) in the Supplement).

3. Results and discussion

3.1. SWAT model performance

It is pointed out from [Fig. 4](#) that the model simulates discharge, suspended solids, nitrate, and total phosphorus satisfactorily following the criteria suggested by [Abbaspour \(2020\)](#). The developed model has a very good performance in daily streamflow simulation where P-factor values are larger than 0.7 and R-factor values are less than 1.2 in both calibration and validation periods. P-factor values of 0.89 and 0.81 mean that 89 % and 81 % of observation data fall within the simulation ensemble in calibration and validation periods, respectively. In addition, R-factor values of 0.61 and 0.2 indicate that the model uncertainty for discharge is reasonably low. The model is found to be reliable also in estimating nitrate, suspended solids, and total phosphorus despite their limited available measured data. As indicated by the R-factor ([Fig. 4](#)), the uncertainties for nitrate, suspended solids, and total phosphorus are larger than discharge because they are involved with more model input uncertainties ([Abbaspour et al., 2007, 2015](#)). Overall, model prediction uncertainty is reasonable and SWAT results are comparable with observed values, and the residual differences between simulation values and measured data reflect both our incomplete knowledge of all catchment processes affecting water flow and nutrient transport, as well as possible errors in the observed data. Nonetheless, our modeling results underline the effectiveness and suitability of the SWAT model in describing hydrology, sediment, and nutrients reported in literature ([Abbaspour et al., 2007; Narsimlu et al., 2013; Anand et al., 2018; Chotpantarat and Boonkaewwan, 2018](#)). Consequently, the SWAT results are further used for evaluating the ecological status of streams in the Albaida Valley.

3.2. Chemical indicators evaluation

Observed ranges of nutrients concentrations at the six sampling sites fall within the ranges predicted by the model, confirming the good performance of the model, except for ammonium concentration at S4; however, no values of ammonium concentration were employed during model calibration, and higher errors are thus expected for this compound ([Fig. 5](#)). As [Fig. 5](#) indicates, the concentrations of chemical indicators vary both in time and space. Chemical characteristics of water differ in the same location over time possibly due to changes in weather conditions, flow regime, and pollution loads in the catchment. In the Clariano River (S1-S9), nitrate concentration increases at S3 due to the effluent of the Ontinyent WWTP, and it then mildly decreases until reaching the Albaida River. Nitrate concentration is lower at upstream sites of the Albaida River (S10-S12), but it increases at the tributary junction (S13). Ammonium concentration in the Clariano River also increases considerably downstream of Ontinyent WWTP (S3), and then strongly decreases (although it remains above the threshold for a good quality status). The Albaida River behaves similarly: ammonium concentration increases downstream of the Albaida WWTP (S11) followed by a decrease until S14 where it slightly worsens because of the effluent of the Alfarrasi WWTP. In the Clariano River, total phosphorus concentration increases significantly downstream of the

Table 4
Ecological status of the Albaida Valley based on mean values of biological and chemical indicators predicted by the model.

site	Biological indicator status	Chemical indicators status	Ecological status
1	Poor	Good	Poor
2	Poor	Good	Poor
3	Bad	Bad	Bad
4	Bad	Bad	Bad
5	Poor	Bad	Poor
6	Poor	Bad	Poor
7	Poor	Bad	Poor
8	Poor	Bad	Poor
9	Poor	Bad	Poor
10	Poor	Good	Poor
11	Poor	Bad	Poor
12	Poor	Bad	Poor
13	Poor	Bad	Poor
14	Poor	Bad	Poor

Ontinyent WWTP and then it is more or less stable. Total phosphorus in the Albaida River also increases downstream of the Albaida and Alfarrasi WWTPs. The simulation results agree with the findings of several field studies reporting the increased concentrations downstream of wastewater treatment systems followed by a progressive reduction with increasing downstream distance from the sources of pollution (Camargo et al., 2011; Menció and Boix, 2018; Camargo, 2019). Overall, the chemical indicators status of the Albaida Valley rivers is often classified as bad (Table 3) except for upstream of streams (i.e., S1 and S2 in the Clariano River, and S10 in the Albaida River). In fact, chemical indicators status considerably changes downstream of WWTPs implying the necessity of WWTPs management.

3.3. IBMWP evaluation

Fig. 6 shows the values of IBMWP predicted for different sites within the streams of the Albaida Valley. The predicted ranges of IBMWP agree very well with values observed at six sampling sites, hence confirming the good performance of the model and the importance of considering probabilistic predictions of biological quality. In the Clariano River, IBMWP decreases considerably at S3 where is affected by Ontinyent WWTP. IBMWP decreases mildly in the Albaida River until the tributary junction (S13) where there is an obvious worsening. Even considering the temporal variability and the model uncertainty, ultimately no site exhibits good biological water quality, which is classified as either poor or bad in most sites. The present results are in line with finding of previous studies on the response of macroinvertebrate community to water quality changes (Camargo et al., 2011; Al-Shami et al., 2011; Mesgaran Karimi et al., 2016; Menció and Boix, 2018). However, these studies are based on measured field data which are limited to space and time. Our innovative approach overcomes this limitation and gives the opportunity to predict the biological responses of streams to several water quality stressors on different temporal and spatial dimensions other than the sampled one through generating time series of macroinvertebrate-based metrics. In particular, this approach complements field studies performed in the Albaida Valley (Martínez Mas et al., 2004; Jiménez and Pérez, 2013; Martínez, 2013).

3.4. Ecological status evaluation

Table 4 presents the ecological status of the Albaida Valley obtained from the model predictions. These results are in agreement with the ecological classification of the Clariano and Albaida Rivers as poor by Martínez Mas et al. (2004) and by Martínez (2013). The present study gives an emphasis to the evident need for mitigation and rehabilitation measures in the Albaida Valley, suggesting that measures such as surface runoff reduction, improvements in WWTPs, modifications of wastewater releases, wetland restoration, regulation of flows (specially to avoid long period of low flow), and management of agriculture could markedly improve environmental conditions of rivers (Nilsson and Malm Renöfält, 2008; Camargo, 2019). It is worth noting that the establishment of realistic thresholds of nutrients is an important component of any nutrient management policy, while some EU member states now employ excessively high nutrient thresholds (Poikane et al., 2021). The approaches suggested for the identification of thresholds for nutrients to support ecological status (Phillips et al., 2018; Kelly et al., 2022) could not be applied in this study because of the limited number of sites and samples. Programming sampling campaigns aimed at this purpose would advance our understanding of nutrient impact on river ecosystems.

4. Conclusions

River ecosystems are extremely impacted by human-induced environmental degradation. Watershed models are beneficial for guiding and evaluating management strategies in such rivers as they are capable of simulating nearly all processes taking place in watersheds in an efficient way. The present study intended to model nitrate, ammonium, phosphorus, and macroinvertebrates as aquatic ecosystem health indicators of the Albaida Valley. This represents an innovative ecohydrological modeling approach that enables us to evaluate temporal and spatial patterns of the ecological status of rivers in the valley. Based on simulated chemical and biological indicators, the ecological status of the valley is mostly classified as poor due to point and nonpoint sources of nutrients. This study recognizes the need for mitigation and rehabilitation measures in the valley, particularly for the management of WWTPs and agriculture. It is concluded that the approach proposed in this study could be used as a complementary technique to river sampling in assessing ecological conditions of rivers. Moreover, the provided approach could be further used to investigate possible impacts of changes in climate, land use, and local management policies on availability and quality of water, and biodiversity.

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. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.ejrh.2022.101155](https://doi.org/10.1016/j.ejrh.2022.101155).

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