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PWC-based evaluation of groundwater pesticide pollution in the Júcar River Basin

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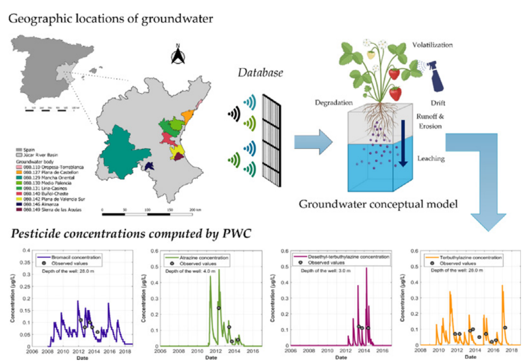
HIGHLIGHTS

- PWC model was used to assess groundwater contamination by pesticides in the Júcar River Basin (Spain).
- Pesticide concentrations in groundwater are higher than 0.10 μg/L. This value exceeds the current Spanish MCL.
- Atrazine and Bromacil were dominant in groundwater.
- Negative effects of pesticides were predicted in the environment.

GRAPHICAL ABSTRACT



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ABSTRACT

Predicting pesticides' behavior in the environment is necessary to anticipate and minimize their adverse effects. Despite the use of pesticides in Spain is increasing, the implementation and use of predictive mathematical models is seldomly done in practice due to the lack of available data. In this original work, the Pesticide Root Zone Model version 5 (PRZM 5) mathematical model under the Pesticide in Water Concentration 1.52 (PWC) interface has been applied to model pesticide behavior in nine groundwater bodies located inside the Júcar River Basin (JRB) in Spain. Mathematical modeling allowed calculating the maximum concentration of pesticides after completing the calibration process. Bromacil, terbuthylazine, atrazine, desethyl-terbuthylazine, and terbumeton concentrations in groundwater were simulated between 2006 and 2019.

Results show that the maximum pesticide concentration value on every well exceeds the current Spanish Maximum Concentration Limit (0.1 μg/L). PRZM 5 was able to reproduce pesticide concentration observations over time despite the limited amount of available data.

This study contributes to assessing environmental risks caused by the use of pesticides inside the JRB and can potentially be applied in other areas of interest.

1. Introduction

By the early 1980s, several groundwater contamination incidents resulting from the field application of pesticides were confirmed (Holden, 1986). Pesticide is any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest or weed (EPA, 2005a, 2005b). Pesticides can be classified according to their target, mode, period of action, or chemistry (Arias-Estévez et al., 2007). Around 200 pesticides are

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currently used in agriculture, and a wide range of hydrogeologic conditions affect the susceptibility of groundwater to pesticide contamination (Aktar et al., 2009).

Pesticide evolution over time results in degradation products that may induce environmental contamination, affecting soil, water, and air over time (Székács et al., 2015) (Schreiner et al., 2016) (Silva et al., 2019). Pesticides cause changes in the physicochemical and biological properties of the agricultural soils, affecting their quality and inducing a negative impact on crop yields (Baxter and Cummings, 2008). Pesticides in groundwater and most residues in surface water usually come from agricultural activities, allowing pesticides to seep into the soil and resulting in groundwater contamination (Younes and Galal-Gorchev, 2000).

In this context, pesticide residues present on the surface can move to the soil and reach groundwater bodies. There are two routes by which pesticides enter the soil: (i) spray drift to soil during foliage treatment plus wash-off from treated foliage (Rial Otero et al., 2003) and (ii) release from granulates applied directly to the soil (López-Pérez et al., 2006).

It is frequent that the concentrations of pesticides exceed the limits established by the legislation in force, which indicates excessive use of these and/or little optimized application methods. In fact, it is estimated that only 0.1 % of the applied pesticides have an effect on pests, fungi, and bacteria since their application is preventive (Pimentel and Levitan, 2014). This excess is subjected to different processes; sorption, degradation, leaching, volatilization, absorption by plants, erosion, runoff, and infiltration into groundwater (Cheng, 1990). Therefore, it is essential to study the dynamics of pesticides in water bodies and soil: sorption–desorption (Arias-Estévez et al., 2005), transport (López-Blanco et al., 2005), and the dependence of transport on entry dynamics and transformation processes.

Pesticide dynamics in the soil are very complex and depend on a number of factors that influence the processes mentioned above. These factors refer to the properties of pesticides (such as solubility and degradation coefficient), soil properties (structure, organic matter, sand, gravel, and clay content), and variables that can be modified throughout the agricultural field (such as hydrological characteristics that vary in space and time).

To predict these dynamics, a series of mathematical models have been developed to take into account the physical, chemical, and biological processes involved, as well as the field-management practices of pesticides (PESTAN (Ravi and Johnson, 1992), EXAMS-PRZM (Burns et al., 1982), SCI-GROW (Barrett, 1997), MACRO (Jarvis and Larsbo, 2012), PFAM (Young, 2013), TOXSWA (Adriaanse, 1996), SWASH (Roller et al., 2015). The objectives of these models are to establish a complete and quantitative image of the temporal behavior of the contaminants in the system by estimating their concentrations over time. Although field measurements are the most reliable way to detect and quantify the presence of pesticides in water, they are limited, so predictive models should be used to evaluate the temporal evolution of contaminants (European Commission, 2003a; Vaz, 2019; Williams et al., 2010). Modeling the environmental fate of pesticides has become an important tool for assessing the risk of water contamination, influencing decision-making by competent authorities (Boesten and Gottesburen, 2000). Several studies use these mathematical models to predict the behavior, mobility, and persistence of pesticides in the environment (D'Andrea et al., 2020; Chen et al., 2017; Huff Hartz et al., 2017; Rumschlag et al., 2019; Sinnathamby et al., 2020; Xie et al., 2018).

Previous studies in Spain have detected the presence of pesticides both in surface water (Belenguer et al., 2014; Ccanccapa et al., 2016a, 2016b; Köck-schulmeyer et al., 2012; Kuster et al., 2008; Masiá et al., 2013; Pitarch et al., 2016; Rousis et al., 2017) and in groundwater (Cabeza et al., 2012; Hernández et al., 2008; Menchen et al., 2017; Postigo et al., 2010).

The groundwater bodies of the Júcar River Basin (JRB) in Spain are located under an area of intense agricultural activity in which the use of pesticides is frequent (CHJ, 2015). In most of the cultivated areas citrus trees are grown, although there are also irrigated zones dedicated to vegetables, as well as dry land areas where cereals, olives, and vines are grown (CHJ, 2018). Groundwater concentrations of pesticides higher than the maximum concentration levels (MCL) have been detected inside the JRB (Environmental Spain Ministry, 2009). Therefore, JRB is an area of interest for the study of these contaminants.

In this work, the software Pesticide in Water Calculator 1.52 (PWC) was used to model pesticide fate in JRB groundwater. PWC allows performing simulations considering a large number of parameters, such as local characteristics of climate, soil, hydrology, and agricultural practices (Young, 2016). In addition to its versatility, this software also stands out for being freely available online and is therefore widely used for the regulation and registration of pesticides (EPA, 2005a, 2005b). Although studies using PWC have been previously published (D'Andrea et al., 2020; Sinnathamby et al., 2020), we are not aware of any previous study for pesticide estimation inside the JRB.

Taking everything above into account, this work has the following two objectives:

(i) to simulate the fate and transport of five pesticides (bromacil, terbuthylazine, atrazine, desethyl-terbuthylazine, and terbumeton), using the PRZM 5 mathematical model under the PWC interface. To achieve this objective, it is also necessary to make a detailed and synoptic description of the study area, to have a deep knowledge of the physicochemical characteristics of pesticides, and to consider actual values of hydrometeorological, hydrogeological, and phenological data.
(ii) to assess and compare the pesticide simulated concentrations with actual values observed in the available wells. To perform this task, a manual calibration process of pesticide applications was conducted, adjusting the value of the parameter "Amount" of the PRZM 5 model, as the exact distribution and applied amount of pesticide in the crops were unknown.

As a result of the overall research, this study demonstrates the possibility of implementation pesticide numerical modeling as a regulatory tool for pesticide groundwater exposure in Spain.

2. Materials and methods

2.1. Description of the study area

The study area (Fig. 1) is located inside the Júcar River Basin (42,700 km^2), in the eastern part of the Iberian Peninsula. JRB shows a semi-arid Mediterranean climate which has favored the establishment of a prosperous agricultural economy. Intense agricultural activity has led to high levels of pesticides in both ground and surface waters (Calvo et al., 2021) (Arias-Estévez et al., 2007) (Andreu and Picó, 2004). In the JRB, the average yearly temperature is 18 °C and the average annual rainfall is 500 mm/year. In dry years, the average annual rainfall is around 250 mm/year, while in wet years this value rises up to 750 mm/year (Fig. 2).

Mathematical modeling of pesticide contamination has been performed in the nine specific groundwater bodies located inside JRB shown in Fig. 1. Ten wells inside these groundwater bodies were not in compliance with the legislation due to high concentrations of different pesticides (Table 1). Pesticide concentration values in these groundwater bodies exceeded the criteria established in accordance with the Royal Decree 1514/2009 (Environmental Spain Ministry, 2009), which states the maximum concentration levels for active substances. Legal reference values in Spain are 0.1 μg/L for a single pesticide and 0.5 μg/L for the sum of all pesticides detected and quantified in the monitoring process.

Supplementary Fig. S1 shows the location of the ten wells within these nine groundwater bodies.

2.2. Identification and characteristics of the pesticides identified in the study area

Resulting from the extensive agricultural activity developed during the last decades, the following five pesticides have been identified inside the

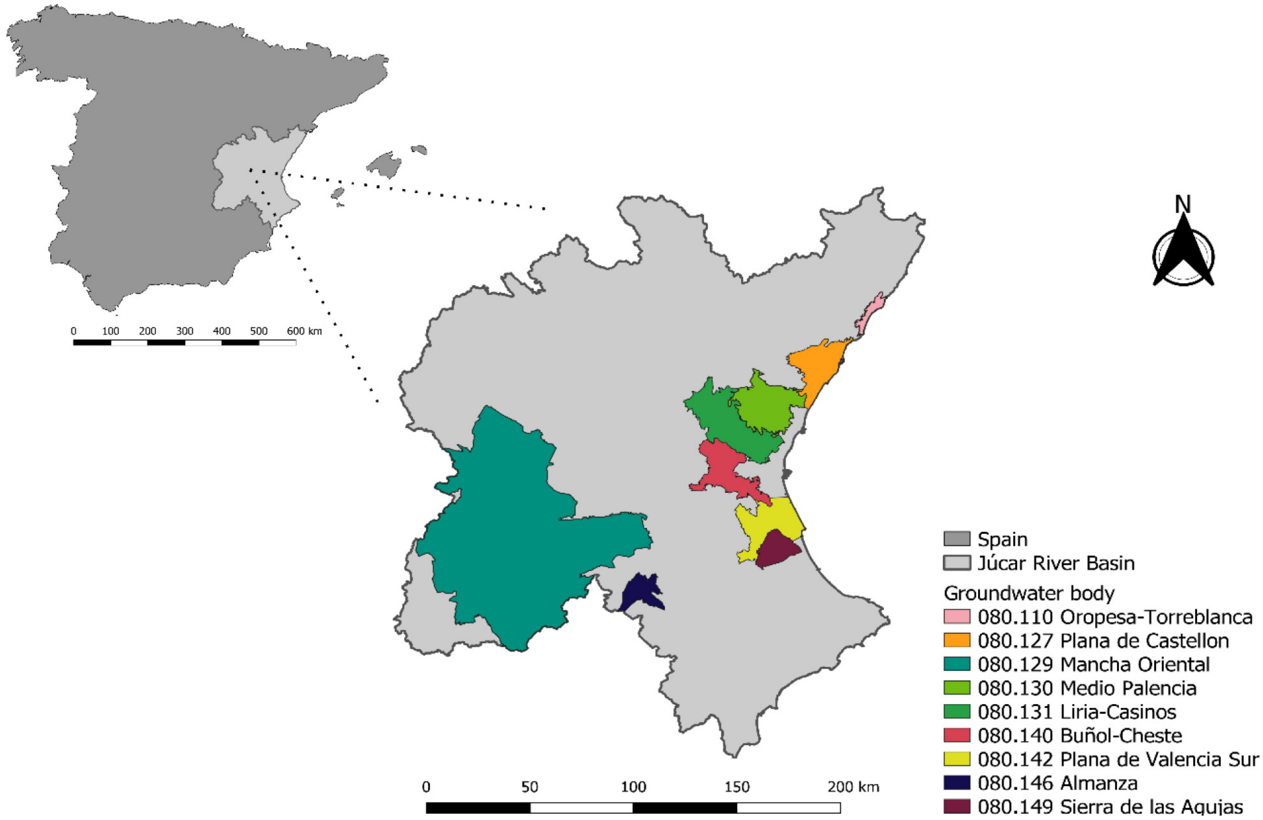

Fig. 1. Location of the nine groundwater bodies analyzed inside the JRB.

study area: bromacil, terbuthylazine, atrazine, desethyl-terbuthylazine and terbumeton. (Pascual Aguilar et al., 2017) (Rodrigo-Ilarri et al., 2020).

Bromacil (5-bromo-3-sec-butyl-6-methyluracil) is one of a group of compounds called substituted uracils (Brycht et al., 2016). It is a systemic, broad-spectrum herbicide used for nonselective weed and bush control on non-cropland areas, as well as for selective weed control on a limited number of crops, such as citrus fruit and pineapple (Chen et al., 2016). These pesticides enter the plant through the root zone and move throughout it inhibiting photosynthesis (Gawel et al., 2020).

Bromacil was first registered as a pesticide in the United States (US) in 1961. Since then, it has been used in a variety of agricultural and non-agricultural situations (James and Lauren, 1995). Bromacil has been included in the list of priority pollutants of the US Environmental Protection Agency (US EPA, 2014). Since it was not included in 2002 in the EU

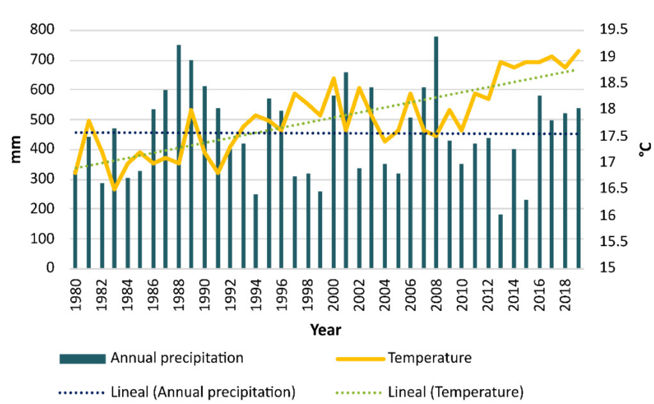

Fig. 2. Evolution of precipitation and temperature in the JRB.

list of approved pesticides, its use is not permitted in any Europe Union (EU) member state (Gawel et al., 2020).

Atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine), firstly developed in 1958, is one of the most widely-used chlorine herbicides in agriculture (Rostami et al., 2021). It is a selective herbicide used to control different broadleaf weeds and grasses in major crops such as maize and sugarcane. Higher application doses of atrazine in non-agricultural lands are recommended for non-selective control of weeds (Dehghani et al., 2013).

Due to their persistence, high mobility and extensive use, atrazine and its derivatives are among the most prevalent herbicides detected in ground and surface waters in agricultural areas (Gawel et al., 2020). A multitude of physical and chemical characteristics, such as high leakage potential and absorption by organic materials and clay, allow atrazine to be quickly transformed from a leading herbicide to a dangerous surface and groundwater pollutant (Graymore et al., 2001; Yu et al., 2020).

Due to the widespread contamination of ground and surface waters, as well as its associated endocrine-disrupting activity, the use of atrazine is banned since 2004 in the US. In the EU, regulations oblige to keep pesticide concentrations lower than 0.1 μg/L in the areas where they are used (European Commission, 2003b; Tasca et al., 2018).

Terbuthylazine (N-tert-butyl-6-chloro-N′-ethyl-[1,3,5]triazine-2,4-diamine), a member of the chloro-*s*-triazine family, has been widely used as a selective herbicide for vegetation management in agricultural and forest production (Tasca et al., 2018; Wang et al., 2010). It was one of the most used herbicides in some EU countries until it was prohibited in 2004 (Álvarez et al., 2016; Oriol et al., 2021). Despite its reduced mobility, due to its low solubility and high adsorption coefficients, terbuthylazine is expected to be retained in the soil during long periods, and therefore inducing lower aquifer contamination risk than atrazine (Jurina et al., 2014; Stipičević et al., 2015). Terbuthylazine is frequently found both in groundwaters and surface waters at levels exceeding the regulatory limits renders (Álvarez et al., 2016; Bottoni et al., 2013;

Table 1
Pesticide identification inside the nine groundwater bodies under analysis.

No. well	Well	Groundwater body	Pesticide
080.110.CA002	Pedrera	Oropesa-Torreblanca	Bromacil
080.127.CA593	Cap del Terme	Plana de Castellón	Bromacil
			Terbuthylazine
080.129.CA004	Rafael Martin Sierra	Mancha Oriental	Atrazine
080.130.CA002	Pozo Maladicha	Medio Palencia	Terbuthylazine
080.131.CA004	Pozo San Antonio	Liria Casinos	Desethyl-terbuthylazine
08.140.CA142	Llano de Cuarte	Buñol-Cheste	Atrazine
			Bromacil
			Terbuthylazine
08.142.CA003	Algadins	Plana Sur de Valencia	Terbumeton
			Desethyl-terbuthylazine
08.142.CA004	Las Salinas		Terbumeton
08.146.CA002	Los Rosales	Almansa	Atrazine
08.149.CA001	Gandía	Sierra de las Agujas	Atrazine
			Bromacil
			Desethyl-terbuthylazine

Tasca et al., 2018). In 2011, the European Food Safety Authority (EFSA) provided an extensive peer review of data concerning environmental behavior and fate, ecotoxicology, mammalian toxicology and risk assessment of terbuthylazine (EFSA, 2011). Based on these conclusions, the European Commission approved the inclusion of terbuthylazine in Annex I of Council Directive 91/414/EEC. The use of terbuthylazine was permitted until December 2021 (European Commission, 2011).

Desethyl-terbuthylazine, together with terbuthylazine-2-hydroxy and terbuthylazine-desethyl-hydroxy, is a main degradation product of terbuthylazine (Stara et al., 2016). The degradation products of pesticides are usually more polar and pose a greater potential risk for groundwater contamination, often with considerably higher toxicity than does the parent compound (Loos et al., 2010).

Terbumeton is a methoxytriazine herbicide (2-amino-4-tert-butylamino-ethyl-6-methoxy-1,3,5-triazine-2,4-diamine), which was primarily used in vineyards (Conrad et al., 2006).

It is more leachable and persistent than other herbicides, such as bromacil and terbuthylazine. The two herbicides that are most commonly detected in groundwater at high concentrations are terbumeton and bromacil. They usually show higher concentrations than terbuthylazine (de Paz and Rubio, 2006). Terbumeton was banned in the European Union by the Commission Regulation (EC) 2076/2002 of November 20th 2002 (European Commission, 2002).

Due to their mobility and persistence in the environment, these five herbicides may induce a high risk of leaching into surface waters and contaminating groundwater bodies (Gawel et al., 2020). The presence of these pesticides in the JRB's groundwater bodies is usually due to the persistence of historical applications carried out before their use was prohibited. An alternative reason is that these pesticides may have been used despite their prohibition by the European legislation, as they are still allowed in other countries and these substances are still marketed.

2.3. The Pesticide in Water Calculator (PWC) model

To perform the mathematical modeling of pesticide concentration in groundwater, the "Pesticide in Water Calculator (PWC)" model version 1.52 has been used (Young, 2016).

PWC model includes the following three components:

1. PRZM 5 - Pesticide Root Zone Model version 5 (Young and Fry, 2016).
2. VVWM - Variable Volume Water Body Model (Young, 2016).
3. A graphical user interface (GUI) that facilitates pre- and post-processing of the input and results.

PRZM 5 is a mathematical model which is used to analyze the movement and degradation of different pesticides, using a one-dimensional finite differences scheme to calculate the fate and vertical transport of pesticides through the vadose zone. The hydrological component for calculating runoff is based on the curve number (USDA, 1986) and the Universal Soil Loss Equation (Smith et al., 2020; Young and Fry, 2016).

VVWM is designed to model the transport and fate of chemical substances in a water body. VVWM simulates hydrological components (evaporation, piezometric level variations and runoff) and pesticide-related components (mass transfer, degradation, absorption), finally estimating pesticide concentrations accounting for all the available data (Young, 2019).

The research work described below was performed to estimate pesticide concentrations in groundwater using PRZM 5.

2.4. Model implementation

The following sections detail how the different modules of the model (tabs) have been implemented in this study. The PRZM 5 model includes four modules related with the chemical properties of the pesticides, the application method used, the characteristics of the crops and the hydrological parameters.

2.4.1. Chemical properties of the pesticides

This study has been focused on all the five pesticides identified inside the observation wells. The physicochemical information of the pesticides was extracted from the Pesticide Properties Database (PPDB) (Lewis et al., 2016). The ranges of concentration values were defined according to the existing literature for each physical-chemical parameter. These values can be found in Supplementary material Table S1.

2.4.2. Application patterns

The study sites were chosen due to their pesticide use and inputs variability (agricultural area, soil group, crop types, application patterns). The calibration process of the pesticide parameter "Amount" has been performed manually, following a trial-and-error process and adjusting the distribution of every pesticide to reproduce the observation data (Pérez-Indoval et al., 2021). The number and dates of the applications were obtained from surveys of farmers performed by the Ministry of Agriculture Fisheries and Food and the Environment (MAPA).[1]

The results of these surveys do not provide information about the exact pesticide doses applied, so their distribution is not known with certainty. Therefore, only ranges of pesticide applications are known, and their final value and their distributions were calibrated after an iterative process that allowed deciding the value of the PRZM 5 parameter "Amount" for each one of the five pesticides. The final amounts of each pesticide applied

[1] https://www.mapa.gob.es/es/estadistica/temas/estadisticas-agrarias/agricultura/estadisticas-medios-produccion.

in each one of the nine groundwater bodies are shown in Supplementary material Table S2.

2.4.3. Crop characteristics

The phenology characteristics of the nine groundwater bodies have been introduced in the model according to the crop distribution shown in Fig. 3. The characteristics of the agricultural units in the study area have been obtained from the JRB's Automatic Hydrographic Information System (SAIH).[2]

On the groundwater bodies of Oropesa, Plana de Castellón, Medio Palencia, Liria Casinos, Buñol Cheste, Plana de Valencia Sur and Sierra de las Agujas the most abundant crops were citrus (72 %), vegetables (10 %) and rice (6 %). Therefore, for these groundwater bodies, the crop considered to perform the PRZM 5 simulations was citrus. Following the information obtained from the Ministry of Agriculture Fisheries and Food and the Environment (MAPA)[3] for the Mancha Oriental and Almanza groundwater bodies, the crops with the greatest area are cereals (43.3 %), grapes (24.5 %), corn (12.4 %), vegetables (10.6 %), and forage (5.6 %). Consequently, the selected phenology values was cereal crops.

The crop dates for emergence, mature, harvest, root depth, canopy (cover, height, holdup) and pan factor were collected from the scenarios (USEPA) and the surveys carried out by the JRB Authority. These parameters are shown in the Supplementary material Table S3.

Soil layers were identified using the geological maps of the Spanish Geological and Mining Institute (IGME) and the well depths were obtained from the available historical records of the JRB's SAIH.

The characteristics of the soil layers can be found in the Supplementary material Table S4.

2.4.4. Hydrological data

Meteorological data required by PWC's hydrologic module are precipitation (cm/day), evaporation factor (dimensionless), maximum temperature (°C), minimum temperature (°C), wind speed (m/s) and solar radiation (ly).

For the construction of the weather files, the nearest weather station was assigned to each well. For the Rafael Martin Sierra well in the Mancha Oriental groundwater body, precipitation data were obtained from station N7P0401, while temperature data were obtained from station N7L0101. Data provided by these stations are available in public records at the JRB's SAIH. The wind speed data were obtained from records of the Spanish National Meteorological Agency (AEMET)[4] and the evaporation factor was calculated using Meyer's formula. The solar radiation data were obtained from the Atlas of Solar Radiation in Spain, using climate data from the EUMETSAT (Sancho Ávila et al., 2012).

All this meteorological information was gathered and integrated as shown in Fig. 4. The weather file required to run PWC was generated with a custom script written in R. This procedure was used for the creation of the ten files, one for each contaminated wells in each groundwater body, as shown in Supplementary material Fig. S2.

Tables S5 and S6 indicate the location of the stations used for each parameter and pesticide.

2.4.5. Evaluation criteria

The Nash-Sutcliffe efficiency (Nash and Sutcliffe, 1970) and Percent BIAS statistics have been used to provide a complete measure of the model's performance (Bennett et al., 2013). Nash-Sutcliffe efficiency (NSE) is a standardized statistic that determines the relative magnitude of the residual variance (noise) compared to the variance of the measured data as show in Eq. (1).

$$NSE = 1 - \frac{\sum_{i=1}^{n} (y_i - \widehat{y}_i)^2}{\sum_{i=1}^{n} (y_i - \overline{y})^2} \tag{1}$$

$$PBIAS = 1 - \frac{\sum_{i=1}^{n} (\widehat{y}_i - y_i)}{\sum_{i=1}^{n} y_i} \times 100 \tag{2}$$

The NSE indicator ranges from $-\infty$ to 1 (1 included, with NSE = 1 optimum value). Values between 0 and 1 correspond to acceptable performance levels, while values below 0 indicate a poor fit. In this study, a 0.5 value of the NSE indicator has been used.

The PBIAS indicator (Eq. (2)) measures the average trend of the simulated data, being higher or lower than the observed data. The optimal PBIAS value is 0, indicating that the average simulated data is equal to the observed data. Values close to 0 indicate an acceptable fit. Positive values indicate model underestimation and negative values indicate model overestimation.

Note that y_i and $\widehat{y}_i$ are the ith observed and predicted values, respectively; $\overline{y}$ is the average of the observed value and n is the sample size.

On the simulation of pesticide fate inside each groundwater body, a composite metric (based on Nash-Sutcliffe efficiency and percent bias) was used to ensure a robust and comprehensive evaluation of the model's performance. The model's performance is improved integrating an accurate parameterization of soil layers, sorption coefficient and calibrating pesticide half-life data.

3. Results and discussion

PRZM 5 has been used to estimate the concentrations of the five identified pesticides in the groundwater bodies of the JRB. The modeling process has been carried out to determine if the origin of groundwater contamination by pesticides comes from their excessive use as a consequence of agricultural activities. The results obtained for each of them are shown below.

3.1. Bromacil concentrations

The evolution of bromacil concentration over time is shown in Fig. 5 for four different observation wells. Experimental field data are marked in gray circles as in Figs. 6–9.

Simulated bromacil concentrations do not show significant differences with field measurements. Model results are satisfactory and simulated valued fit observations in the wells. The model predicts the date on which the maximum simulated concentrations are observed in the field. For example, bromacil concentration observed on May 14th 2014 was 0.8 μg/L and the model accurately reproduces this concentration (Fig. 5D).

The model also approaches the effect of an increasing concentration on October 1st 2013 (1.38 μg/L) while the concentration measured in the lab was 1.60 μg/L. On the other hand, the Llano de Cuarte well (Fig. 5C) shows a concentration difference between simulated and measured values equal to 0.13 μg/L. Therefore, the model overestimates the first field concentration in order to simulate the other maximum observed concentrations.

Relations between bromacil concentrations and well depth have been observed. The lower the depth of well, the higher the maximum detected concentration of this pollutant. For example, for the Cap del Terme well, which is 28 m deep, the model simulated a maximum concentration value equal to 0.1913 μg/L (Fig. 5A), being the least contaminated well by bromacil. However, the Pedrera well (depth = 8 m) has a maximum simulated concentration of 0.4380 μg/L. The Gandía well, which has the highest concentration in the simulation (2.4449 μg/L) is only 3 m deep. This relation between well depth and maximum concentration of bromacil has been observed in wells with similar lithological characteristics. These results cannot be generalized and used for wells located in other types of soil.

[2] http://aps.chj.es/down/html/descargas.html.
[3] https://www.mapa.gob.es/es/agricultura/estadisticas/.
[4] http://www.aemet.es/es/portada.

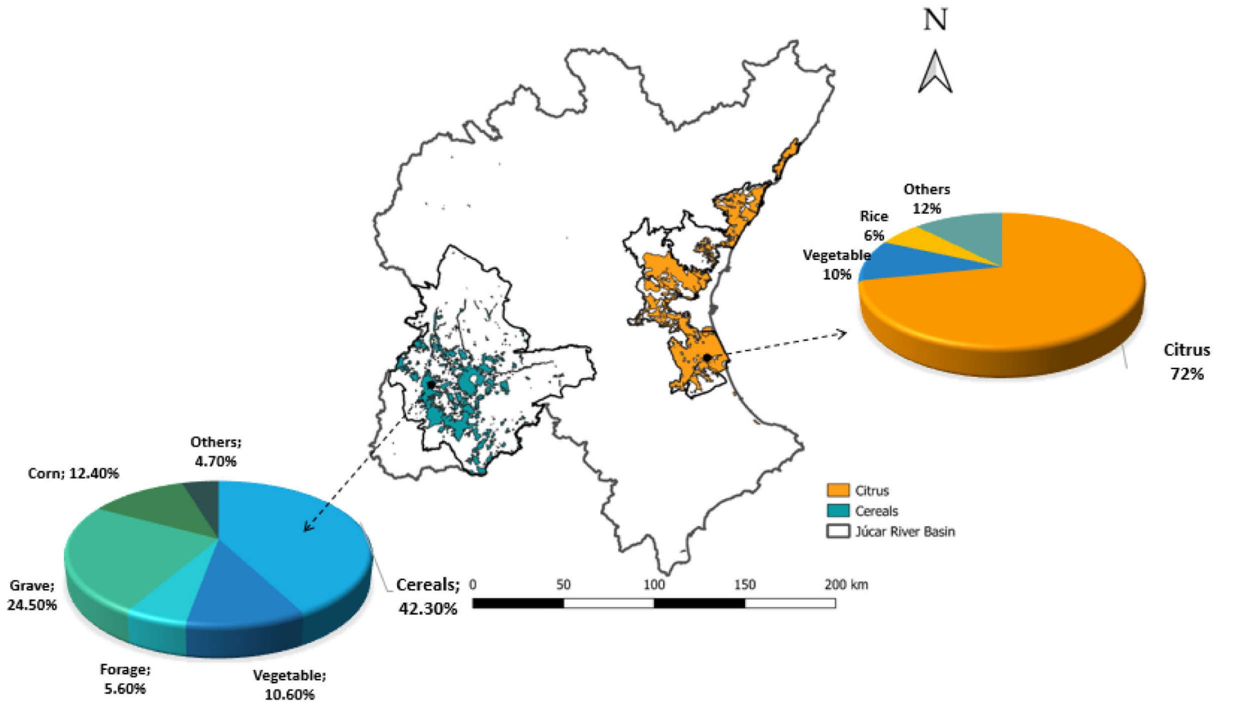

Fig. 3. Distribution of crops in the JRB.

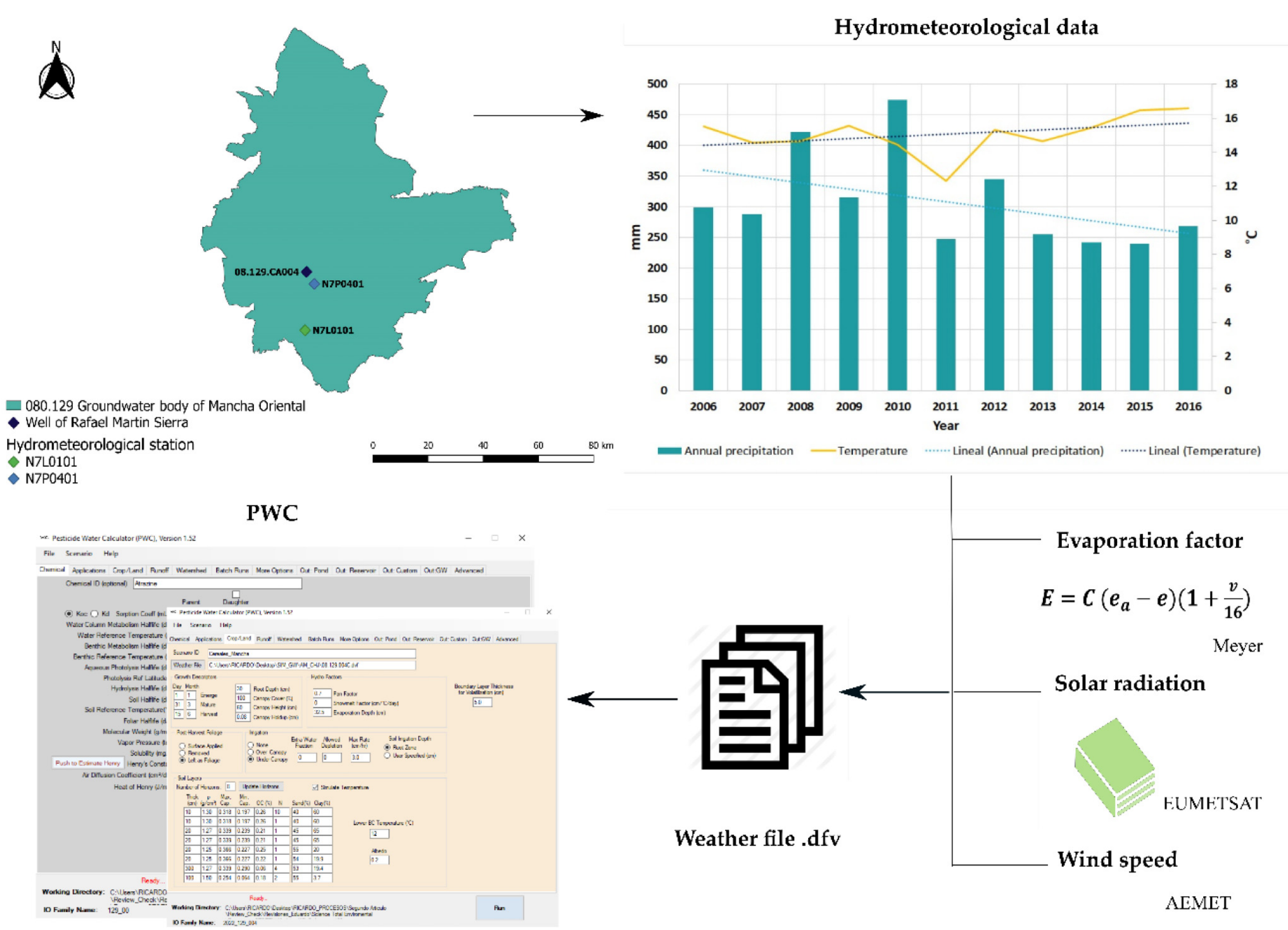

Fig. 4. Structure of the weather file for running PWC.

Fig. 5A shows a different effect in the breakthrough curve of bromacil in groundwater. This effect is an early breakthrough time. The initial time for which the effect of bromacil is first detected in the groundwater is also high, covering a range from 630 days (Fig. 5C) to 1360 days (Fig. 5B). We believe that this effect is due to the fact that the soil profile was modeled with a succession of thin layers up to 1 m thick, whose components are a mixture of clay and sand, and then by a 27 m layer with 80 % sand. This layer is very permeable and facilitates the movement of the pesticide.

3.2. Atrazine concentrations

The temporal evolution of atrazine is graphically represented in Fig. 6 for four different observation wells. Results show that PRZM 5 simulations accurately reproduce atrazine concentrations observed in the observation wells and their evolution, both in short and long periods. In the Rafael Martin Sierra well (Fig. 6A), the simulation period of atrazine concentrations ranges from 2011 to 2015. The use of a 5-year series has been sufficient to calibrate the model parameters on a daily scale. During this period of time, there is hydrological variability and almost no meteorological data are missing. In the Llano de Cuarte well (Fig. 6D), the simulation period of atrazine concentrations is 10 years (2008–2018). In this case, ten field concentrations of atrazine are used as opposed to only four in the other wells (Fig. 6A, B, and C). It has been observed that the model results reproduce better the more recent measurements.

A high persistence index of atrazine has been observed in some of the groundwater bodies. The atrazine persistence time in groundwater varies from 1270 days (Fig. 6A), 1640 days (Fig. 6C) to 2660 days (Fig. 6B).

Fig. 6D shows higher atrazine concentrations (35.00 % of the simulated concentration values are above MCL). Between 2012 and 2018, average concentrations ranged between 0.20 μg/L. Fig. 6B and D shows that atrazine concentrations oscillate around 0.10 μg/L, being this the reference value. The magnitude of this oscillation is dependent on the soil type and the value of the application of pesticide.

3.3. Terbuthylazine concentrations

The temporal evolution of terbuthylazine is graphically represented in Fig. 7 for three different observation wells. The simulated concentration values of terbuthylazine are low in comparison with the other pesticides analyzed in these locations, but still close to the MCL. Concentration values are above MCL during approximately 400 days, as shown in the breakthrough curves (Fig. 7A). However, for well 080. 130.CA002 Sondeo Maladicha, the concentrations are above the MCL during 2350 days.

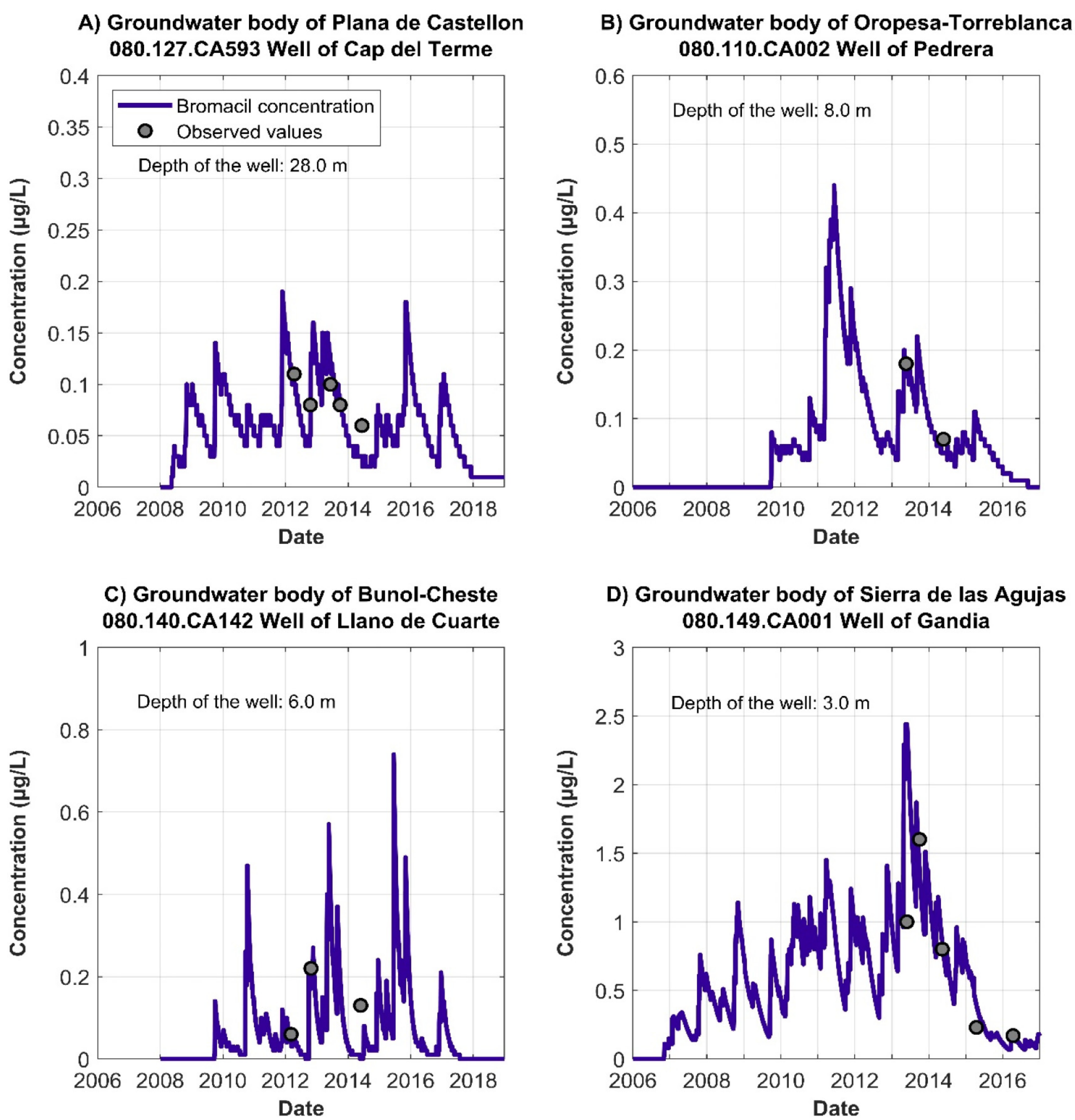

Fig. 5. PRZM 5 simulation results. Bromacil concentrations in four wells.

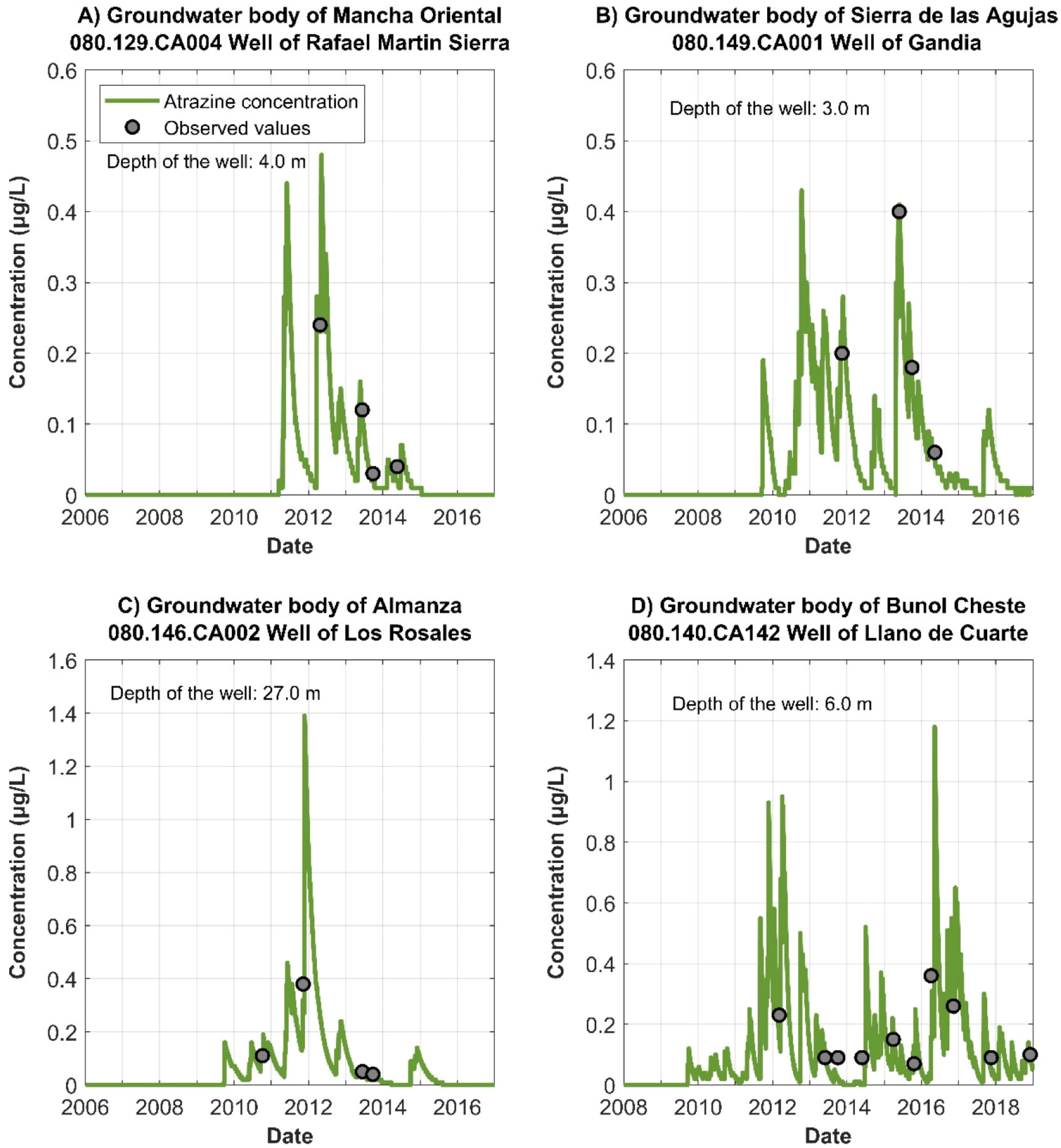

Fig. 6. PRZM 5 simulation results. Atrazine concentrations in four wells.

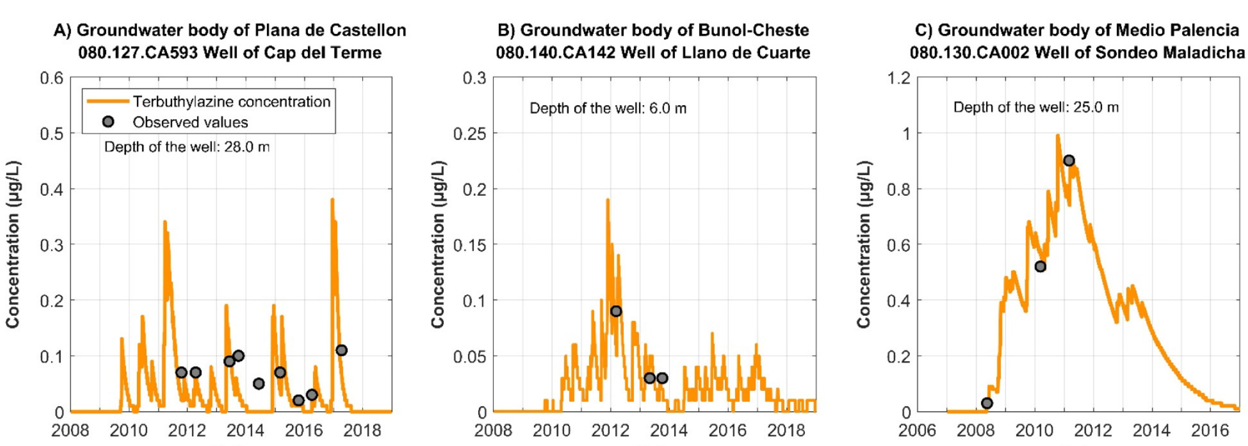

Fig. 7. PRZM 5 simulation results. Terbuthylazine concentrations in three wells.

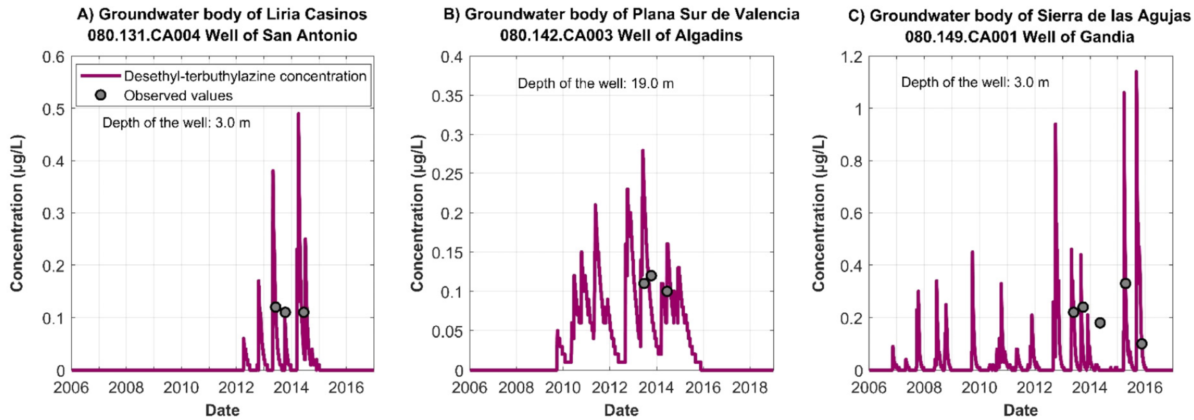

Fig. 8. PRZM 5 simulation results. Desethyl-terbuthylazine concentrations in three wells.

The peak concentration values in the graphics are dependent on the soil type. The wells located in a clay-loam soil type, like Cap del Terme (Fig. 7A) and Llano de Cuarte (Fig. 7B), show lower simulated terbuthylazine peak concentration in comparison with the Maladicha well (Fig. 7C). The clay-loam soil type has a low value of organic carbon, but a higher percentage of clay (35 %) than sand. On the other hand, the sand content in the soil of Maladicha is the highest (66 %). This fact may explain that the maximum values of the pollutant are found in this well. The physical properties of the soil drastically affect the dynamic of the pollutant and its ulterior persistence in subsurface waters. Sandier soils are more permeable and, therefore, facilitate the movement of the pollutant, thus reaching the aquifer faster. Soils richer in clay and organic carbon result in a higher persistence time of the pollutant in the soil and, consequently, lower contamination peaks in groundwater bodies.

3.4. Desethyl-terbuthylazine concentrations

The temporal evolution of desethyl-terbuthylazine is graphically represented in Fig. 8 for three different observation wells. Although it has not been possible to simulate perfectly the observed series of desethyl-terbuthylazine concentrations, model simulations reproduce the peak concentrations observed in the field. For example, Fig. 8A shows that the peak concentration was observed on June 4th 2013 (0.12 μg/L) and the model reproduces this measurement accurately. However, the observed concentration of desethyl-terbuthylazine on October 10th 2013 and June 12th 2014 do not fit the simulated results. This discrepancy may be explained by the existence of additional factors that influence the pesticide movement and that are not incorporated into the model.

Besides, the breakthrough curve shapes for desethyl-terbuthylazine shown in Fig. 8 are similar and have a cyclical behavior, initially increasing until reaching the peak value and dramatically decreasing to zero afterward. In order to visualize and understand the "spiky" breakthrough curves of desethyl-terbuthylazine, the application dates for the simulations were selected within the possible application periods in relation to the planting date. Therefore, the same application dates were used for each simulated year. This pesticide application period varies for each well and pesticide tested. Consequently, the breakthrough curves of desethyl-terbuthylazine behave in a cyclical way once the amount of pesticide applied has been calibrated. When applying similar annual doses of pesticide in the simulation period, the impact of desethyl-terbuthylazine on groundwater quality shows different maximum and minimum values inside each groundwater body. The initial time during which the effect of desethyl-terbuthylazine is first detected in groundwater is highly variable, ranging from 210 days (Fig. 8C) to 1930 days (Fig. 8B).

3.5. Terbumeton concentrations

The temporal evolution of terbumeton is graphically represented in Fig. 9 for two different observation wells. The range of terbumeton concentrations is very different in the two analyzed wells. In Fig. 9A the simulation

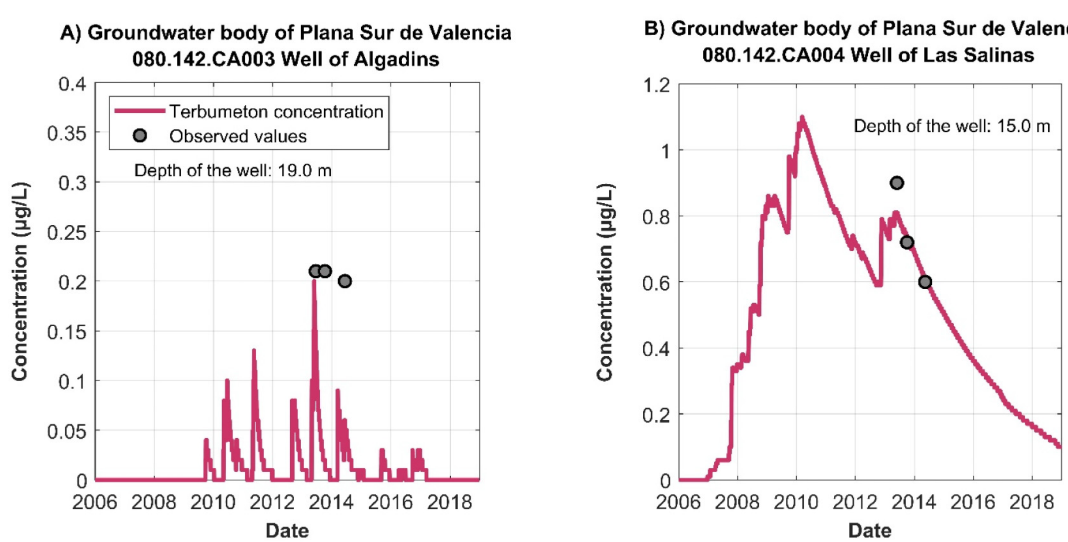

Fig. 9. PRZM 5 simulation results. Terbumeton concentrations in two wells.

covers a range from 0.05 μg/L to 0.15 μg/L, while in Fig. 9B the values have a much wider range, with concentration values exceeding 1.00 μg/L. When comparing Fig. 9A and B, it is verified that the concentrations of terbumeton are four times higher in the Las Salinas well than in the Algadins well. Furthermore, not only the maximum values of pesticide concentrations in groundwater are different, but also the shape of the breakthrough curves. These differences may be due to the effect of different precipitation, which helps the pesticide to mobilize or infiltrate more quickly. In episodes of more intense rainfall, the soil is washed in such a way that an important part of the pesticide retained in the soil is mobilized, increasing the amount of terbumeton that reaches the aquifer. It must be remembered that weather conditions were different in each well.

The simulated relative maximum values of pesticide concentrations occur at almost the same instant. Despite crops may have the same phenology, the spatial-temporal variation effect of terbumeton in JRB groundwater bodies may be due to the fact that the amount of pesticide applied may vary over time. For example, the annual dose of pesticide applied in the Las Salinas well is 3.2 kg/ha, while in the Algadins well it is <2.0 kg/ha.

Fig. 9B shows that the simulated concentrations require a much longer time to reach the peak value, and once this maximum value has been reached, concentration values oscillate over time. It has been seen that simulated concentrations are equal to observed concentrations with a slight difference in the second observed value in Fig. 9A.

A previous approach to the problem addressed in this work was made by (Rodrigo-Ilarri et al., 2020), who proposed one of the first mathematical assessments of pesticides in the DHJ using two numerical models: PESTAN and PRZM-GW version 1.07. These models were used to explain terbuthylazine behavior in the non-saturated zone of a vertical soil column. Numerical simulations show that PRZM-GW was able to reproduce concentration observations leading to much more accurate results than those obtained using PESTAN.

However, this approach was mainly oriented to the assessment of terbuthylazine in a single groundwater body of the DHJ. Results shown now in this work have been obtained for 5 pesticides: bromacil, atrazine, terbuthylazine, terbumeton, and desethyl-terbuthylazine in 10 groundwater bodies of the DHJ, using the PRZM 5 mathematical model under the PWC interface. PRZM 5 takes into account some parameters which are not considered by PESTAN which play a relevant role in the particular case of pesticide evaluation. PRZM 5 is versatile and allows the introduction of a large number of locally- or regionally-specific parameter values. Besides, PWC is a software which is freely available online, and it is widely used for pesticide regulation and registration in the United States and Canada (Rumschlag et al., 2019) (Sinnathamby et al., 2020) (Smith et al., 2021).

Table 2
Summary of the evaluation results of the model.

Well	Pesticide	Peak concentration (simulated)	NSE	PBIAS
Gandía	Atrazine	0.4304	**0.99**	3.57
Los Rosales	Atrazine	1.3936	**0.94**	13.34
Rafael Martin Sierra	Atrazine	0.5083	**0.94**	10.59
Maladicha	Terbuthylazine	0.9894	**0.93**	7.15
Pedrera	Bromacil	0.4380	**0.93**	8.00
Gandía	Bromacil	2.4449	**0.91**	6.77
Las Salinas	Terbumeton	1.0989	**0.82**	3.15
Cap del Terme	Terbuthylazine	0.3789	**0.65**	39.18
Algadins	Terbumeton	0.2838	**0.60**	7.69
Llano de Cuarte	Terbuthylazine	0.1937	**0.56**	18.92
Gandía	Desethyl--terbuthylazine	1.1434	**0.54**	33.83
Cap del Terme	Bromacil	0.1913	**0.20**	13.95
Llano de Cuarte	Atrazine	1.1802	**0.18**	20.92
Llano de Cuarte	Bromacil	0.7356	**−0.35**	34.15
Algadins	Desethyl--terbuthylazine	0.1978	**−59.00**	36.36
San Antonio	Desethyl--terbuthylazine	0.4872	**−86.00**	29.41

This work with PRZM 5, included inside the PWC was crucial to promote and help develop the use of pesticide fate modeling for environmental risk assessment in Spain and also for other countries such as Brazil (De Oliveira Kaminski and Vieira, 2021) and Argentina (D'Andrea et al., 2020).

3.6. Evaluation criteria

For every simulated well, the following variables were evaluated: peak concentration, Nash-Sutcliffe Efficiency (NSE) and PBIAS (Table 2). According to the NSE values, most of the analyzed pesticide-well combinations resulted in an excellent result (NSE > 0.9), while the performance of the model was unacceptable (< 0.5) in 5 pesticide-wells combinations: San Antonio (desethyl-terbuthylazine), Algadins (desethyl-terbuthylazine), Llano de Cuarte (bromacil and atrazine), Cap del Terme (Bromacil). There are many reasons that may cause this lack of linearity between the observed and the predicted data, being one the relatively small variation in the observations. Besides, the Sorption Coefficient parameter (K_{oc}) has not been obtained from reliable data, but from estimates taken from existing literature. This fact suggests the need to obtain solid information on this parameter to simulate the behavior of pesticides using PRZM 5.

Finally, it would be very useful to have more experimental data taken in the observation wells, both in relation to the parameter values related to the application of pesticides and to the physicochemical parameters of the pesticides in the different conditions existing in the study area.

3.7. Environmental impact assessment and recommendations

The concentration of the five pesticides in the most affected years (2012 and 2013) is shown in Figs. 10 and 11, respectively. According to these results, Llano de Cuarte and Gandía wells are the most contaminated wells in the study area. The Llano de Cuarte well shows higher atrazine concentrations than those of terbuthylazine and bromacil. The simulated mean concentration values for terbuthylazine never exceed 0.15 μg/L, while bromacil predicted mean values above 0.25 μg/L.

Results show a higher amount of atrazine concentration for the year 2012, being 56 % of the simulated concentration values above the legal limit (0.1 μg/L).

Besides, the concentrations of bromacil and desethyl-terbuthylazine were higher than the concentrations of atrazine in Gandía well. This could be linked to the agricultural activity, like citrus crops, for which pesticide applications are more frequent. An interesting fact is that the average atrazine and bromacil concentrations in this well are more than two times higher in 2013 than in 2012. This effect may be due to the fact that the model provides results that are just proportional to the amount of pesticide, so the values of the concentration curve is proportional to this dose.

In order to improve the performance of the model in the groundwater bodies of the JRB the following research lines are proposed:

- Model performance may be improved by measuring actual soil horizon data and integrating meteorological data obtained from local weather stations.
- Further research should be performed to improve the calibration of sensitive parameters such as hydrolysis half-life, soil half-life and sorption coefficient.
- Model calibration may be improved if more measurements of pesticides in groundwater bodies were available.

4. Conclusions

This paper shows the results obtained by evaluating the concentrations of five existing pesticides in nine groundwater bodies of the JRB (Spain) using the PRZM 5 mathematical model under the PWC interface. The model simulations were based on the use of pesticides and hydrometeorological data measured from 2006 to 2018. PWC has been used with the PRZM 5 calculation module, which provided results for concentrations of bromacil,

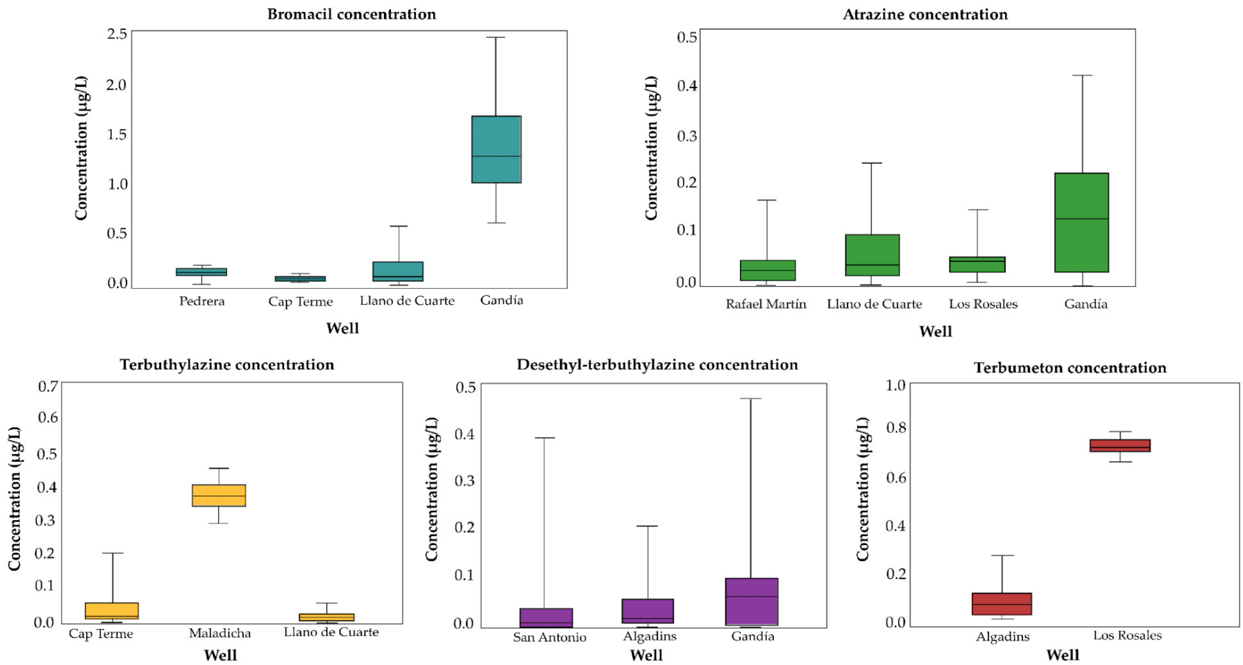

Fig. 10. Boxplots depicting annual pesticide concentrations in 2012: (blue) bromacil, (green) atrazine, (orange) terbuthylazine, (purple) desethyl terbuthylazine, and (pink) terbumeton. The central horizontal line represents the median, and the vertical bars represent the maximum and minimum values of the distribution. The outliers are not represented.

terbuthylazine, atrazine, desethyl-terbuthylazine, and terbumeton in groundwater that were consistent with the observed data.

In most cases, simulated concentrations exceeded the current MCL in Spain (0.10 µg/L) showing that JRB is subject to the entry of pesticides from agricultural applications and is currently at high risk of contamination.

In this work, a large amount of information has been compiled and specific tools have been developed to facilitate the mathematical modeling of pesticides in the JRB's groundwater bodies. The original information that has been produced during the development of this work includes:

(i) a set of databases of climate, soil, and crop phenology according to the parameters required by the model,
(ii) data related to the dimensions and physicochemical characteristics of the JRB groundwater bodies,

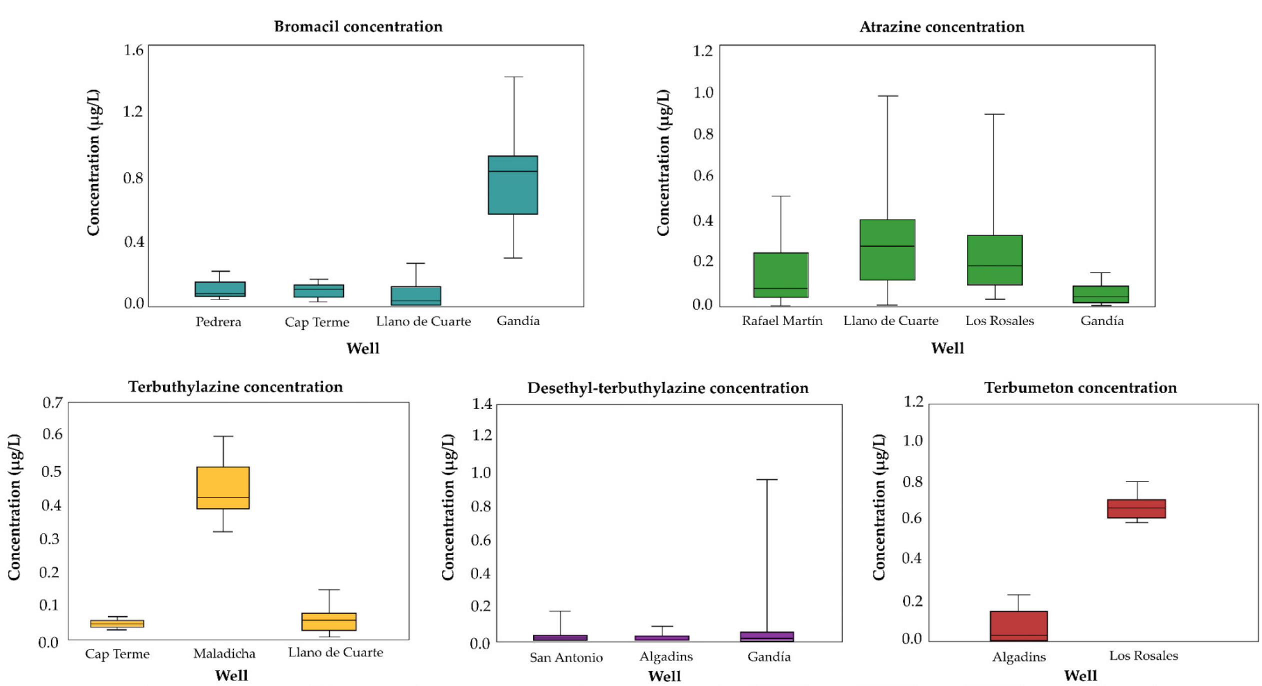

Fig. 11. Boxplots depicting annual pesticide concentrations in 2013: (blue) bromacil, (green) atrazine, (orange) terbuthylazine, (purple) desethyl terbuthylazine, and (pink) terbumeton. The central horizontal line represents the median, and the vertical bars represent the maximum and minimum values of the distribution. The outliers are not represented.

(iii) data related to the physicochemical characteristics of the pesticide to be modeled,
(iv) data on the amount of pesticide (kg/ha) applied to the soil and.
(v) use of the PRZM 5 model to estimate the annual concentration values of each pesticide detected.

The mathematical simulations carried out in the JRB groundwater bodies indicate that the amount of pesticide applied to the soil is the most relevant parameter in the simulation of the concentration of pesticides in groundwater. Therefore, it was decided to perform the calibration of this parameter manually.

In addition, simulation results indicate that pesticide concentrations are highly dependent on other parameters, such as the soil adsorption coefficient, the pesticide half-life in the soil, and the parameters related to the application of the pesticide.

Future pesticide transport modeling research should consider multiple sources of contamination. Thus, the results obtained will help to optimize pesticide application rates to avoid groundwater contamination. This work demonstrates that the PRZM 5 model is capable of simulating different pesticides and soil types present in the JRB. This is the first step in identifying where future modeling efforts in the basin could be directed.

CRediT authorship contribution statement

Ricardo Pérez-Indoval: Writing – original draft, Data curation, Resources, Investigation, Conceptualization, Methodology, Software, Validation, Formal analysis, Visualization. **Javier Rodrigo-Ilarri:** Supervision, Writing – review & editing, Resources, Conceptualization, Methodology, Validation. **Eduardo Cassiraga:** Supervision, Writing – review & editing, Resources, Conceptualization, Methodology, Software, Validation. **María-Elena Rodrigo-Clavero:** Writing – review & editing, Investigation.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.157386.

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