



**Global change  
impacts on Mancha  
Oriental groundwater**

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This discussion paper is/has been under review for the journal Hydrology and Earth System Sciences (HESS). Please refer to the corresponding final paper in HESS if available.

# Integrated assessment of the impact of climate and land use changes on groundwater quantity and quality in Mancha Oriental (Spain)

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Received: 1 July 2014 – Accepted: 7 August 2014 – Published: 17 September 2014

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Published by Copernicus Publications on behalf of the European Geosciences Union.

## HESSD

11, 10319–10364, 2014

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## Abstract

Climate and land use change (global change) impacts on groundwater systems cannot be studied in isolation, as various and complex interactions in the hydrological cycle take part. Land-use and land-cover (LULC) changes have a great impact on the water cycle and contaminant production and transport. Groundwater flow and storage are changing in response not only to climatic changes but also to human impacts on land uses and demands (global change). Changes in future climate and land uses will alter the hydrologic cycles and subsequently impact the quantity and quality of regional water systems. Predicting the behavior of recharge and discharge conditions under future climatic and land use changes is essential for integrated water management and adaptation. In the Mancha Oriental system in Spain, in the last decades the transformation from dry to irrigated lands has led to a significant drop of the groundwater table in one of the largest groundwater bodies in Spain, with the consequent effect on stream-aquifer interaction in the connected Jucar River. Streamflow depletion is compromising the related ecosystems and the supply to the downstream demands, provoking a complex management issue. The intense use of fertilizer in agriculture is also leading to locally high groundwater nitrate concentrations. Understanding the spatial and temporal distribution of water availability and water quality is essential for a proper management of the system. In this paper we analyze the potential impact of climate and land use change in the system by using an integrated modelling framework consisting of the sequentially coupling of a watershed agriculturally-based hydrological model (SWAT) with the ground-water model MODFLOW and mass-transport model MT3D. SWAT model outputs (mainly groundwater recharge and pumping, considering new irrigation needs under changing ET and precipitation) are used as MODFLOW inputs to simulate changes in groundwater flow and storage and impacts on stream-aquifer interaction. SWAT and MODFLOW outputs (nitrate loads from SWAT, groundwater velocity field from MODFLOW) are used as MT3D inputs for assessing the fate and

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found in the results. Section 4 summarizes the conclusions that can be drawn from the case study and the methodology used, and clearly states the contribution of this work to the climate and land use change impact assessment.

## 2 Materials and methods

### 2.1 Case study: the Mancha Oriental system in Spain

The Mancha Oriental system (MOS) is located in an area of semiarid climate in the southwestern part of the Jucar River Basin, mainly within the Albacete province, Spain (Fig. 1). The study area covers about 8400 km<sup>2</sup> consisting on plains surrounded by ranges that delimitate the borders between the Jucar, the Tajo (Tagus), the Guadiana and the Segura river basins. The northern area is dominated by three main rivers: the perennial Jucar river and the seasonal Valdemembra and Ledaña rivers. The southern portion is a former endorheic plain which was artificially connected to the Jucar river in the XIX century by the Maria Cristina Channel. The main land use of the area is agriculture, being especially characteristic the circular-shaped groundwater-irrigated crop areas, devoted mainly to corn, wheat and barley. A detailed geological description can be found in Sanz (2003) and Sanz et al. (2009, 2011).

In the last 25 years, an important transformation from dry to irrigated lands has taken place in La Mancha, in central Spain, with the development of an intensive agriculture that represents one of the main factors in the current economic development of the region. More than 80 000 ha of lands equipped with modern technologies are currently irrigated, regarded as one of the most important in Spain, with most of these lands depending on groundwater. The main crops are wheat, corn, barley and alfalfa, with a significant share of the crop production still dependent of CAP subsidies, and with some growing areas of vegetables and vineyard. The aquifer has been subject to intensive groundwater pumping during the last decades (since the 70's), which has resulted in a continued drop of groundwater levels, especially in its southern

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groundwater management issues, as decreasing groundwater recharge is likely to increase the pressure on the quantity and quality status of the Mancha Oriental aquifer.

## 2.2 Climate change scenarios

The climate change scenarios rely on the SRES A1B emission scenario for Europe. Climate data predicted were obtained from three different GCM drivers: CNRM (National Centre of Meteorological Research), ECHAM5-r3 (European Centre for Medium-Term Weather Forecast), and HADCM3-Q0 (Hadley Centre). These scenarios have been downscaled using the SMHIRCA 3.0 RCM (Regional Climate Model) of the Swedish Meteorological and Hydrological Institute (SMHI). This study is one of the 16 case studies in the GENESIS Project, which deals with climate and land use impacts on groundwater and dependent ecosystems. For all case studies, the same dynamic downscaling method was applied by the GENESIS Project partner SMHI, which provided the meteorological forcing time series for the climate change scenarios (Kjellstrom et al., 2011; Nikulin et al., 2011). Daily time series of the relevant meteorological variables were provided for the 1961–2100 period, corresponding to a control period (1961–1990), and the short-term (2010–2040), medium-term (2040–2070), and long-term (2070–2100) scenarios.

A comparison was made for the control period (1961–1990) between the climate scenarios and the historical time series, in order to check if they were reproducing the observed patterns in the main statistics of temperature and precipitation. Historical data was obtained from the Spanish Meteorological Agency (AEMET). The comparison of monthly averaged means and standard deviations for maximum temperature and precipitation can be seen in Fig. 2. With regard to maximum temperatures, the ECHAM5 scenario is the one whose monthly means better resemble the historical pattern, being the CNRM scenario the one located further from the observations. Regarding standard deviations of monthly temperature, all scenarios showed lower values, especially during summer, with no remarkable differences between them. Figure 2 also shows differences on the mean precipitation monthly pattern, especially in

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April and September. No climate change model was adequately reproducing the winter observed precipitation. CNRM and HADCM3 scenarios seemed to be more close to the observed data from January to August, but the ECHAM5 scenario appeared to be more adequate after August. The same situation was found regarding the standard deviation comparison between scenarios and observed data.

The temperature and precipitation series for the three climate scenarios are shown in Fig. 3, which depicts the 10 year moving average values. There is a steady increase in temperature, with a decreasing trend in precipitation, more accused in the long-term. The other meteorological variables provided (relative humidity, solar radiation and wind speed) did not show any clear trend. Finally, CO<sub>2</sub> concentrations were obtained from the carbon cycle models ISAM and BERN, both used in the IPCC Fourth Assessment Report climate projections. A concentration value of 421.67 ppmv was considered for the short-term period, while concentrations of 531.67 and 665.50 ppmv were considered for the mid and long-term respectively.

### 2.3 Land use change projections

Land use change is a complex process dominated by a large number of variables. In order to adequately assess the effects of the global change, land use change must be added to the changes related to climatic variables, coupling the climate change scenarios with the projected land use changes, whose driving forces belong to different categories of social, economic, political, human and natural factors. Four land use change scenarios (LUCS) have been considered in this case study, each one with regard to different time periods

- LUCS-1: short-term scenario based on a multi-temporal analysis of historical LUC changes and their key drivers, future EU scenarios and a combination of LUC allocation techniques.
- LUCS-2: medium-large term scenario considering persistence of the main LUC evolution trend observed in the last 20 years, being characterized by a change



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from the available literature and statistical data with spatial representativeness (INE, 2011) from a wide range of biophysical, social, economic and political factors. A set of 20 driving forces were finally selected and spatially represented in GIS format (raster), using a Cramer's V test to select relevance of each driving force in every transition with a threshold value of 0.15 (Eastman, 2006). Table 1 shows the driving forces selected.

Markov chains and European scenarios and projections (Eururalis 2.0 and Image 2.2) have been used to quantify trends in the future. The EU project Eururalis 2.0 (Klijn et al., 2005) was chosen because its focus on rural areas. Eururalis developed Europe's future land-use scenarios for 2010, 2020 and 2030 (Westhoek et al., 2006; Rienks, 2007); all available on-line to assist decision makers on the most likely scenarios of the Common Agricultural Policy (CAP). Predictions of LULC future scenarios are obtained through a combination of suitability maps and transition probability matrices extracted from all data sets described. Multicriteria Evaluation (MCE) method using Artificial Neural Networks (ANN) was performed to obtain suitability maps (Oñate-Valdivieso and Bosque Sendra, 2010) where change could happen for each transition selected. Multilayer Perceptron (MLP) with three layers, backpropagation of error algorithm and the sigmoid transformation function were used to train every ANN. Transition probability matrices (TPM), based on Markov's chain theory, express the probability of one LULC to change to another in a determined period of time. TPM were obtained from historical data and from Eururalis land-use scenarios. Applying the Markov process theory to the historical data (2000–2006), transition matrices for the 2000–2010 period were derived. For 2000–2020 period, transition matrices were obtained from the tendencies showed by the Eururalis scenario. Finally, cellular automata algorithm fed with suitability maps of every transition and transition probability matrices produced the final suitability maps and land-use scenarios. A detailed explanation of the methodology can be found in Henriquez-Dole (2012).

## 2.4 Modelling framework

Numerical simulation models provide the most effective way to estimate the impacts of climate and land use changes on water quantity and quality of groundwater systems. In order to assess the impacts of the assumed future conditions (climate, land use, water demands, adaptation, etc.) on groundwater systems, some forms of coupling need to be assumed between those forcings and hydrogeology. This requires the practical integration of operational models that not only represent all of the relevant processes in the hydrologic system in a physically meaningful way, but are also simple enough to allow large-scale basin-wide applications (Sophocleous and Perkins, 2000).

Different processes of the hydrologic cycle need to be modeled and integrated. The characterization of the land phase of the hydrological cycle is essential for assessing the impacts of climate and land use changes on the temporal and spatial distribution of groundwater recharge and contaminant loadings. Moreover, in basins in which irrigated agriculture is a dominant land use, as in our case study, we also need to involve calculations of plant growth and crop yields, crop ETs, irrigation applications and groundwater pumping changes. Another additional requirement in this case was to include simulation of nitrate leaching from the crop fertilization, in order to assess impacts of future scenarios on groundwater nitrate pollution. The tool selected for this purpose was SWAT. The Soil and Water Assessment Tool (SWAT) is one of the most widely used watershed model worldwide, applied extensively to a broad range of scales and environmental conditions (Gassman et al., 2007, 2014).

While the distributed SWAT model is capable of properly reproduce the spatio-temporal distribution of groundwater recharge rates (at the spatial resolution given by their hydrologic response units), its groundwater module is lumped; therefore, distributed parameters (such as hydraulic conductivity and storage coefficient) cannot be represented, and the approach and is very limited for expressing the spatial distribution of groundwater levels and groundwater flow dynamics (Kim et al., 2008).

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percolation, runoff, and return flow components. Every process included in the model can be solved using different methodologies. In our case, the surface runoff derived from daily rainfall is estimated with a modification of Soil Conservation Service (SCS) curve number method (included in the model). The percolation through each soil layer is predicted using storage routing techniques combined with crack-flow model (Arnold et al., 1995). The evapotranspiration was estimated using Hargreaves formula. Finally, the flow routing in the river channels is computed using the variable storage coefficient method (Williams, 1969).

SWAT uses a single plant growth model to simulate all types of land cover and differentiates between annual and perennial plants. The plant growth model is used to assess removal of water and nutrients from the root zone, transpiration, and biomass/yield production (Arnold et al., 2012). Planting, harvesting, tillage passes, nutrient and pesticide applications can be simulated for each cropping system with specific dates or with a heat unit scheduling approach. The irrigation applications can be simulated for specific dates or with an autoirrigation routine, which triggers irrigation events according to a water stress threshold.

The nitrogen (N) processes and soil pools simulated by SWAT are described in Neitsch et al. (2002). SWAT monitors five different pools of N in the soil. Two of them are inorganic forms of N:  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . The other three are organic forms of N: fresh organic N associated with crop residue and microbial biomass, and the active and stable organic pools associated with the soil humus. SWAT is capable to simulate N fixation by legumes, fertilizer inputs and nitrogen in the rainfall as well.

The SWAT model for the Mancha Oriental system (MOS) has been fed with the following inputs, divided into four categories: DEM, climate data, soil data and land use data.

The Digital Elevation Model (DEM) used in SWAT has a 670 m  $\times$  670 m cell size, being used to delimitate a total amount of 35 sub-basins (using the ArcSWAT watershed delineator tool) and to derive the slope map.





Once the model's HRUs have been created, the crop management (quantity of applied fertilizer, the seedtime, irrigation and harvest timetable; the water source, hydric stress threshold, etc.) must be introduced in the SWAT model, due to its influence in the hydrologic process. Crop management parameters were based on normal practice of farmers in the watershed.

## 2.6 Groundwater flow model

MODFLOW is a fully distributed model that solves the three-dimensional groundwater flow equation using finite-difference (FD) approximations. The model calculates the hydraulic head at each cell of the FD grid (for which the aquifer properties are assumed to be uniform), and from there, the flow between cells, stream-aquifer or lake-groundwater interaction, flows through drains etc. The model requires geological and hydrogeological aquifer information such as top and bottom layer elevations, hydraulic parameters at the grid (hydraulic conductivity, storage coefficient), as well as the boundary and initial conditions and stresses.

The MOS groundwater model consists of 7 hydrogeological units (HU), three of them are considered as aquifers (HU2, HU3 and HU7) and the other as aquitards (Sanz et al., 2011, 2009). The hydrogeological unit 7 is present throughout the MOS and is composed of limestone and fractured dolostone. The HU3 is only present in the northeast part of the study area and is composed of fractured limestone and dolostone. The upper aquifer, the HU2, which is located in the central part is composed of an alternate sequence of marl-lime and marl. Six hydrogeological domains can be identified in the MOS: Northern (ND), Central (CD), El Salobral-Los Llanos (SLD), Moro-Nevazos (MND), PozoCañada (PCD) and Montearagón-Carcelén (MCD) domains. According to Sanz (2009, 2011) there is hydraulic connection between the ND, CD and SLD domains, but not between MND, PCD and MCD or among these three and ND, CD and SLD. The Jucar River is the most important surface body and it is hydraulically connected to the aquifer, mainly to the HU2.

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SWAT outputs. Only agricultural sources were considered. Since only few scattered measured values of nitrate concentrations were available for calibration, the calibration mainly consisted in matching the maximum nitrate concentrations simulated with the ones reported in Moratalla et al. (2009).

### 3 Model calibration and validation

In the proposed modelling framework, given the sequential use of models, the SWAT, MODFLOW and MT3D models were calibrated independently; the modelling chain was then tested with the observed values.

#### 3.1 SWAT calibration

The SWAT calibration procedure has followed four sub-processes, consisting on river flow, groundwater recharge, crop yield and nitrate leaching calibrations. A preliminary sensitivity analysis was run using the SWAT-CUP software (Abbaspour, 2012), obtaining that the most sensitive parameters of the model were the SCS Curve Number (CN2), the groundwater discharge coefficient ( $\alpha$ ), the travel time coefficient from soil to shallow aquifer, the inverted flow coefficient that is finally lost due to evaporation, and the two primary evapotranspiration parameters. That sensitivity analysis also showed that the CN2 and  $\alpha$  parameters were, by far, the most sensitive ones. The fact that the CN2 parameter was the most sensitive enhances the importance of combined climate and land use change analyses in the Mancha Oriental aquifer.

Two river gauging stations have been selected to calibrate the SWAT model's hydrology. The first one, Los Frailes (08036 station), is located at the very center of the case study zone, close to the Jucar and Valdemembra rivers confluence. The second one, Alcalá del Júcar station (08144), is placed downstream of the confluence between Jucar and Ledaña rivers, and therefore, downstream the reach of stream-aquifer connection within the Mancha Oriental aquifer. Figure 1 shows the location

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characteristic (including initial NO<sub>3</sub> concentration), and other factors such as the percolation factor affecting NO<sub>3</sub> transport.

In order to find out if the SWAT model performance is adequate, its nitrate leaching values have been compared with ones provided in previous studies about nitrate leaching from agriculture in the region (Martin-Benlloch, 2012) (Table 2). In addition, nitrogen leaching estimates were also tested through comparison of the resulting simulated groundwater nitrate concentration from MT3D with the observed values. Given the usual absent of data, the calibration and validation of nitrate loads is often based on observed nitrate concentrations in surface gauging stations and observed groundwater nitrate concentrations (e.g. Mariela et al., 2011; Amon-Armah et al., 2013; Laurent and Ruelland, 2011; Narula and Gossain, 2013).

### 3.2 MODFLOW

MODFLOW calibration has been carried for the same period as the SWAT model (1994–2004 period), using 24 piezometers. Figure 7 graphs the calibration results obtained in 8 piezometers located in different parts of the Mancha Oriental aquifer. The model performance closely resembles the historical records at the observation wells and, therefore, the MODFLOW model has been adequately calibrated.

### 3.3 MT3DMS

The MT3D model calibration was hindered by the lack of data, especially by the lack of a continuous time series with at least one record per month. The initial concentration values were interpolated from data reported in the literature (Moratalla et al., 2009). The nitrates entering the aquifer were calculated using the SWAT model, whose leaching calibration process has been showed. Since only few scattered measured values of nitrate concentrations are available for calibration, the calibration consisted in matching the maximum nitrate concentrations simulated and their spatial distribution pattern with the ones reported in the literature (Moratalla et al., 2009).

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and, during some periods, the groundwater tables offered by the LUCS-3 scenarios are located below the LUCS-2 ones. To sum up, the land use change scenarios effect on groundwater levels is higher than the climate change one. The lower amount of pumping associated to the LUCS-3 scenarios leads to higher groundwater levels.

5 However, general declines can be noticed for the whole scenarios. The oscillations noticed in the series evolution are associated to climate variability, adding an important source of uncertainty to the results.

### 4.3 Impacts on groundwater quality

Groundwater quality impacts of climate and land use changes have been analyzed in terms of groundwater nitrate concentrations using the MT3DMS model.

10 Nitrate leaching results from SWAT runs are showed in Fig. 10. Higher values of nitrate leaching are obtained for the scenarios based on the CNRM model (GC09 to GC16), associated to higher precipitations that originate higher groundwater recharge. The scenarios associated with the LUC-2 land use change scenario (the largest irrigated areas) are generally the ones with higher nitrate leaching values, while the LUCS-4 offer the lower bound of nitrate leaching values, indicating a synergic effect between climate and land use change. Differences between land use change scenarios become significant in the medium and long term. The decreasing precipitation and recharge plays a beneficial effect in the nitrate leaching, being reduced in all the future scenarios.

20 MT3DMS results are showed in Fig. 11. Nitrate concentrations in the Mancha Oriental aquifer increase in nearly all the observation points. Nitrate change concentration trends match with the expected behavior, showing an increase over the century, with the highest concentrations for the LUCS-2 scenario. There is no agreement between the points in the time period that shows higher concentration increases, but the majority of them show the steepest increases at the end of the XXI century, driven by the recharge reduction previously noticed. All the climate change and land use change scenarios show the same evolution trend for a particular point.

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Oriental aquifer and to the whole Jucar River Basin, as this aquifer plays an important role in the Jucar middle-basin streamflows, especially regarding the fact that the aquifer status is not good at this moment. Despite the recent stabilization of groundwater abstractions, the expected reduced recharge from climate change projections will add additional pressure on the sustainability of the groundwater system. Increasing streamflow depletion in the Jucar river would decrease the amount of water available downstream, increasing conflicts for meeting downstream demands and environmental requirements. In order to avoid these and other potential future threatens, the new Jucar River Basin Management Plan include a program of measures to prevent further groundwater level depletion and enhance groundwater heads recovery, in order to achieve a good quantitative and chemical status in the Mancha Oriental aquifer as required by the EU Water Framework Directive. Global change poses an additional hurdle to this intended program of measures, as changing patterns would decrease the aquifer's natural recharge and would force to further develop a robust of adaption of to ensure sustainable groundwater use.

Regarding these premises, several conclusions of this case study should be made:

- Global change must be taken into account in the planning and assessment of the management policies for a sustainable development of the Mancha Oriental system, as the results obtained without considering global change impacts are likely to be too optimistic
- The currently intended program of measures regarding the MOS must be re-assessed in order to:
  - Check the effectiveness of this program of measures under climate global conditions
  - Redefine the program of measures to adapt to global change conditions

Participatory processes engaging the relevant stakeholders are essential in the successful definition and implementation of sustainable adaptation measures for

groundwater management, and techniques as the Multi Attribute Value Theory, already applied to the case study (Apperl et al., 2014) can be very useful for ranking measures based on the stakeholder preferences and values and for anticipating potential conflicts among competing uses.

5 Finally, climate and land use changes impact not only groundwater levels and groundwater discharge to the river, but also groundwater quality. Increasing groundwater nitrate concentrations can be anticipated due to the continuous intense use of fertilizers in agriculture over time. Economic instruments might have an essential role in enhancing a sustainable management of diffuse pollution for the future (Peña-Haro et al., 2014).

*Acknowledgements.* This study has been partially supported by the European Community 7th Framework Project GENESIS (226536) on groundwater systems as well as from the Plan Nacional I+D+i 2008–2011 of the Spanish Ministry of Science and Innovation (Subprojects CGL2009-13238-C02-01 and CGL2009- 13238-C02-02).

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**Table 1.** Selected driving forces for the Mancha Oriental land use change.

Biophysical factors	Distance to rivers Distance to lakes Mean annual precipitation (Thiessen) Mean annual temperature (Thiessen) Slope Digital Elevation Model (DEM) Orientation Soil type (organic matter proportion) Proximity to flooding zones
Social Factors	Distance to urban agglomerations Distance to towns Population density in 2003 (municipal level) Population growth rate (1996–2003) at municipal level
Economic and Political factors	Distance to local roads Distance to regional roads Distance to national roads Distance to pumping extraction plants Location of agriculture zones Belonging to a specific province Belonging to the Mancha Oriental Aquifer



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**Table 2.** Crop irrigation, crop and nitrate leaching management calibration.

Crop type	Irrigation (mm)		Yield (Tn ha <sup>-1</sup> )		Leaching (kg NO <sub>3</sub> ha <sup>-1</sup> )	
	SWAT	ITAP	SWAT	ITAP	SWAT	GEPIC
Wheat	363	350–420	7.2	7–8	53	45–85
Onion	572	550–620	5.1	4.5–5.5	114	100–120
Corn	552	500–600	12.2	12–13	100	90–115
Sugarbeet	827	800–900	12.8	12.5–13.5	74	65–90
Barley	282	250–350	8.6	8–9	34	30–45
Alfalfa	782	750–850	12.1	11.5–12.5	12	10–30

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**Table 3.** Analysis scenarios.

Scenario	Climate Change scenario	Land use scenario	Period
GC01	ECHAM5	LUCS-1	Short-term
GC02	ECHAM5	LUCS-2	Mid-term
GC03	ECHAM5	LUCS-2	Long-term
GC04	ECHAM5	LUCS-3	Mid-term
GC05	ECHAM5	LUCS-3	Long-term
GC06	ECHAM5	LUCS-4	Short-term
GC07	ECHAM5	LUCS-4	Mid-term
GC08	ECHAM5	LUCS-4	Long-term
GC09	CNRM	LUCS-1	Short-term
GC10	CNRM	LUCS-2	Mid-term
GC11	CNRM	LUCS-2	Long-term
GC12	CNRM	LUCS-3	Mid-term
GC13	CNRM	LUCS-3	Long-term
GC14	CNRM	LUCS-4	Short-term
GC15	CNRM	LUCS-4	Mid-term
GC16	CNRM	LUCS-4	Long-term
GC17	HADCM3	LUCS-1	Short-term
GC18	HADCM3	LUCS-2	Mid-term
GC19	HADCM3	LUCS-2	Long-term
GC20	HADCM3	LUCS-3	Mid-term
GC21	HADCM3	LUCS-3	Long-term
GC22	HADCM3	LUCS-4	Short-term
GC23	HADCM3	LUCS-4	Mid-term
GC24	HADCM3	LUCS-4	Long-term

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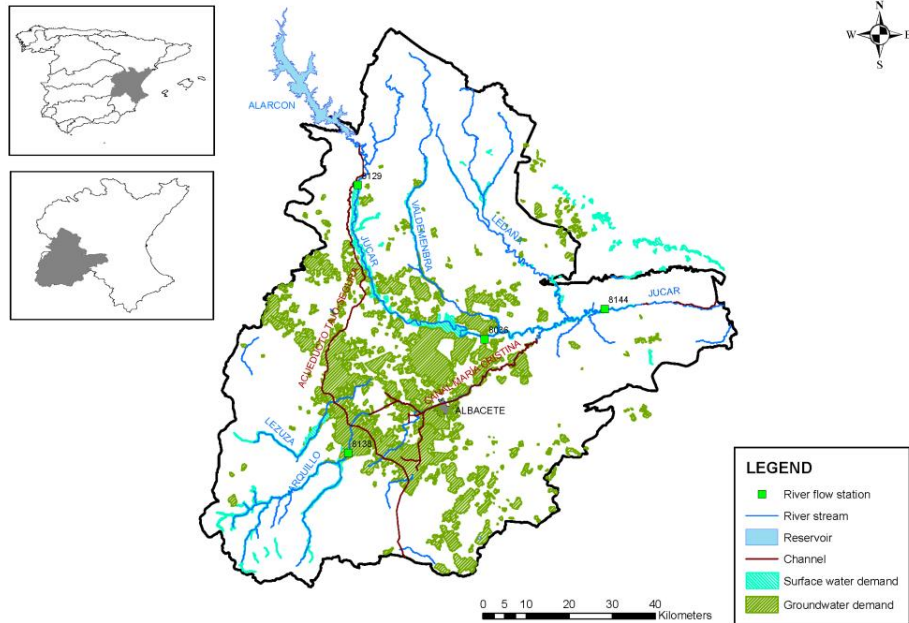
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M. Pulido-Velazquez  
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Period	Average temperature (°C)			Average precipitation (mm)		
	ECHAM5	CNRM	HADCM3	ECHAM5	CNRM	HADCM3
Historical	18.0	19.3	17.6	417.6	412.2	408.5
Short term	18.9	20.2	19.1	375.8	408.1	367.6
Medium term	20.4	21.4	20.8	338.2	379.2	339.1
Long term	22.0	22.4	21.8	279.8	346.3	347.2



**Figure 1.** Mancha Oriental Aquifer location map.

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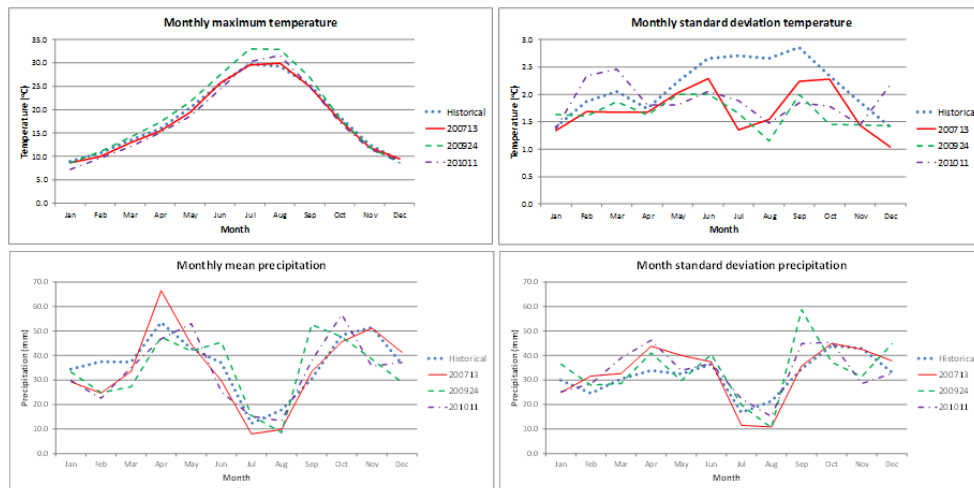
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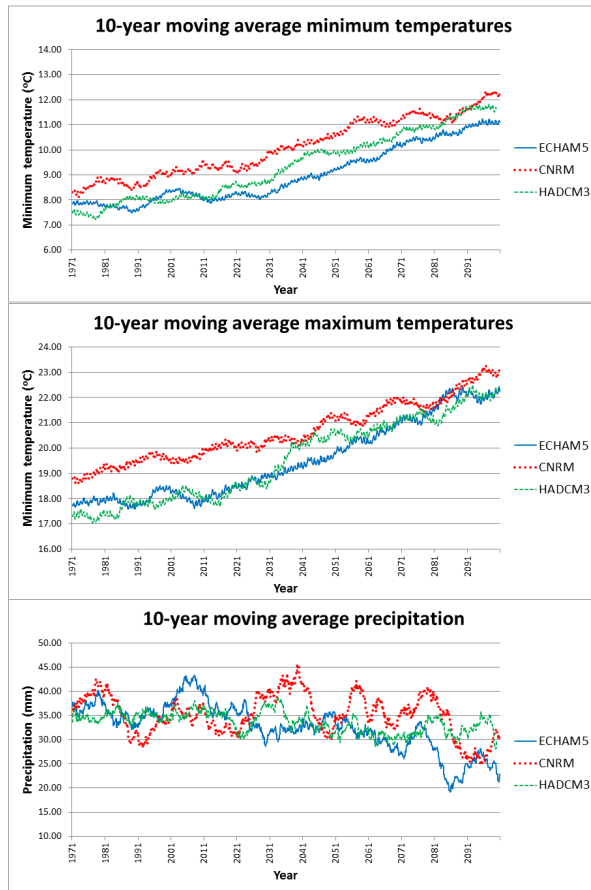
**Figure 2.** Monthly mean and standard deviation comparison on temperature and precipitation.

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**Figure 3.** Temperature and precipitation 10 year moving average values for the climate change scenarios.

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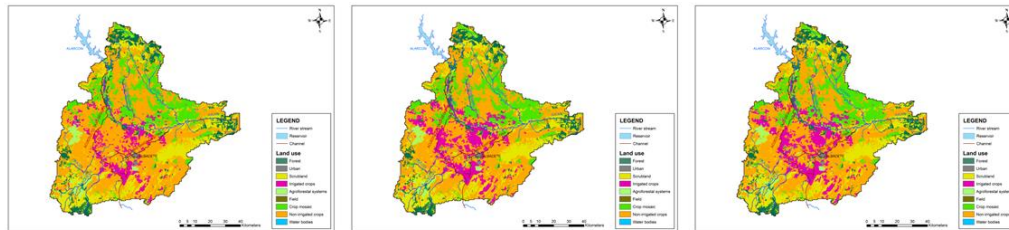


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**Figure 4.** CORINE Land Cover images for years 1990, 2000 and 2006 in the Mancha Oriental Aquifer.

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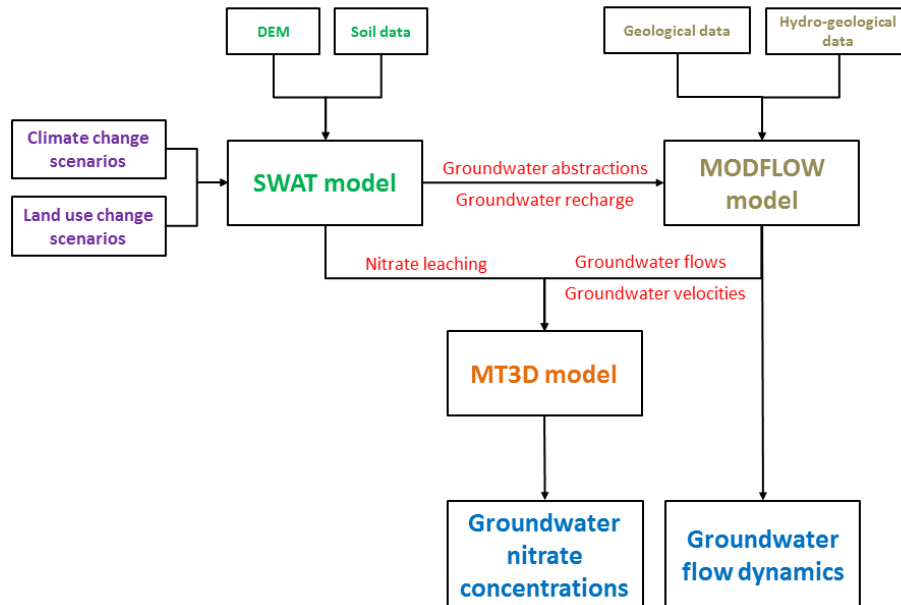
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**Figure 5.** Modeling framework adopted.

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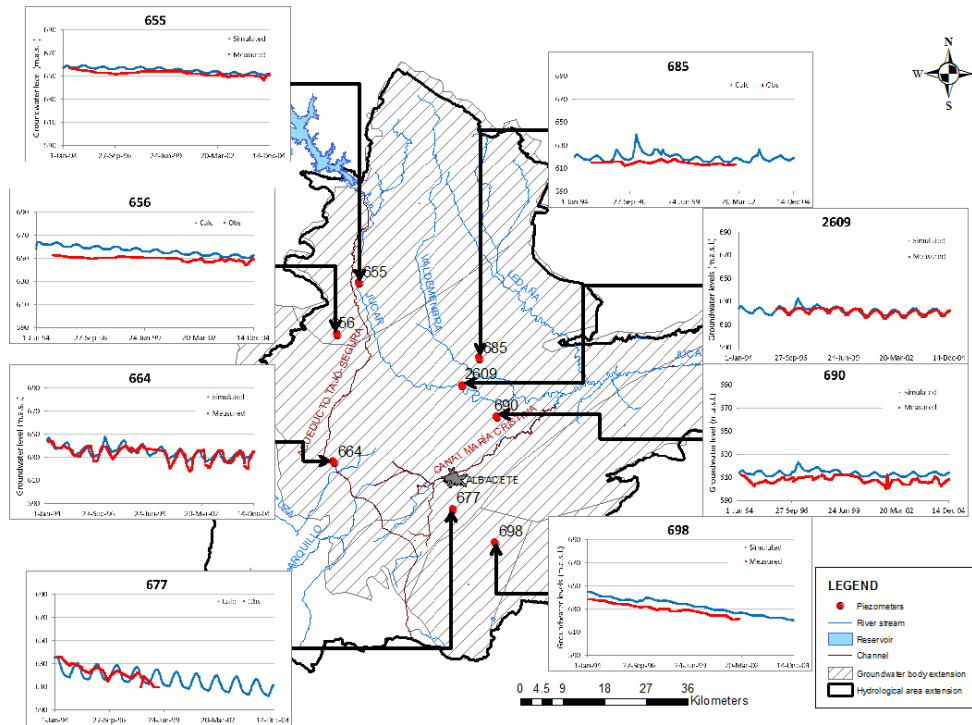


Figure 7. MODFLOW model calibration.

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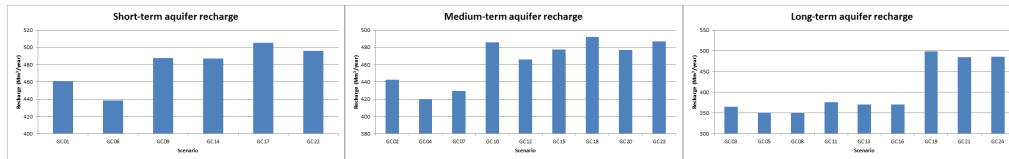


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**Figure 8.** Groundwater recharge results obtained with SWAT for the short-term (left), medium-term (middle) and long-term (right).

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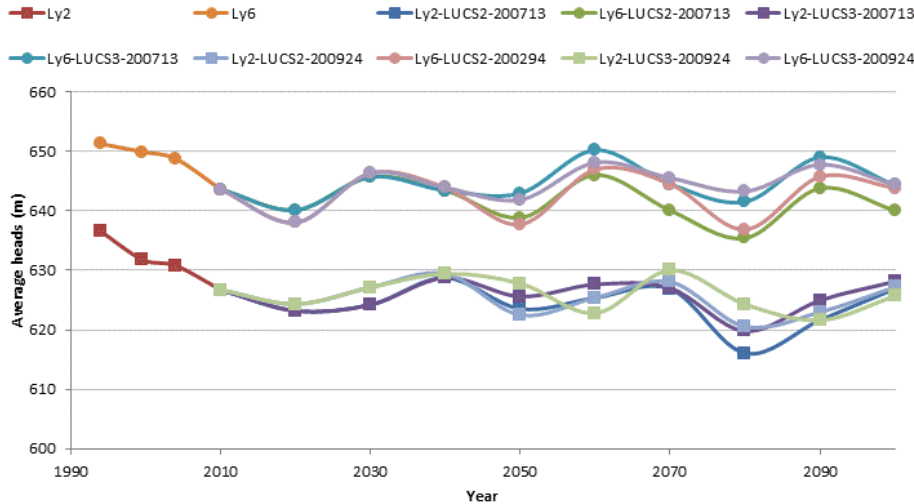


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**Figure 9.** Groundwater level evolution during the XXI century of layers 2 and 6 of the Mancha Oriental Aquifer.

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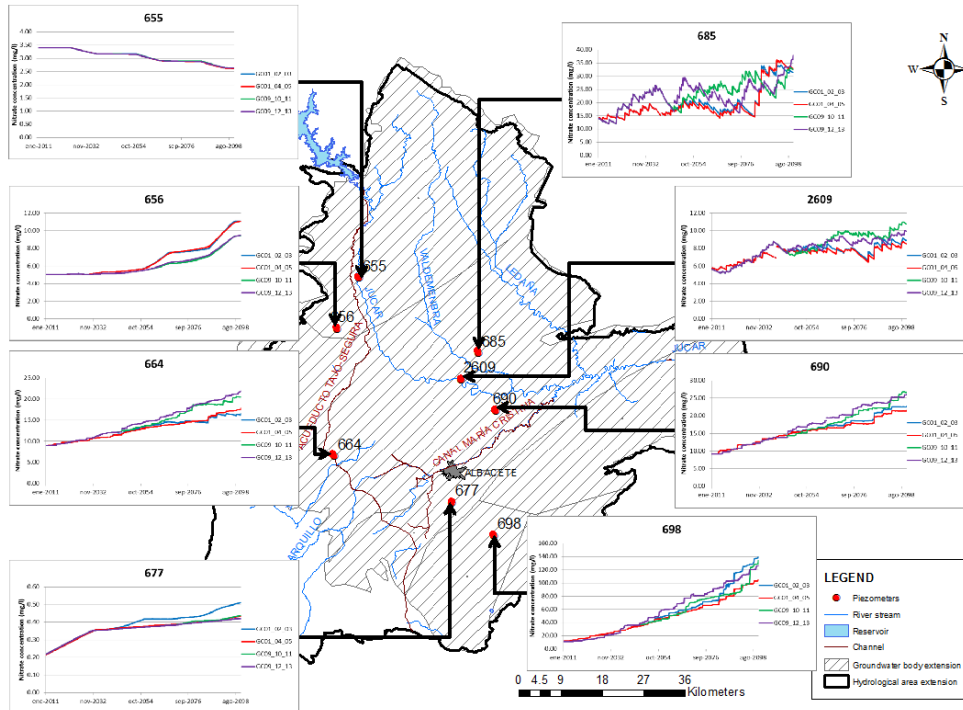
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**Figure 11.** Nitrate concentration evolution in the Mancha Oriental aquifer obtained with MT3DMS.