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Pérez-Martín, MÁ.; Estrela Monreal, T.; Amo-Merino, PD. (2016). Measures required to reach the nitrate objectives in groundwater based on a long-term nitrate model for large river basins (Jucar, Spain). *The Science of The Total Environment*. 566:122-133.  
doi:10.1016/j.scitotenv.2016.04.206



The final publication is available at

<https://doi.org/10.1016/j.scitotenv.2016.04.206>

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Additional Information

# **Measures required to reach the nitrate objectives in groundwater based on a long-term nitrate model for large river basins (Júcar, Spain).**

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**Keywords:** *Water Nitrate; Groundwater; Water Framework Directive; Large River Basin; Mediterranean; Nitrogen Pollution.*

## **Abstract**

Nitrate pollution, primarily in groundwater (GW), has been one of major water pollution problems in Europe over the last 30 years. Specially, Mediterranean areas (semi-arid zones) are more vulnerable to nitrate pollution, as in these areas a small excess of nitrogen produce higher nitrate concentrations than in more humid countries because the aquifer recharge is minor. A large number of GW bodies in the Júcar River Basin District (RBD) (43.000 km<sup>2</sup>), located in Spain, has nitrate concentrations above 50 mg/L. The Water Framework Directive (WFD) sets out the goal of good status for the water bodies of the European Union, which also implies compliance with the Nitrates Directive.

The River Basin Authorities (RBAs) must define the measures needed to reach the environmental objectives in the River Basin Management Plans (RBMPs), considering the long time-lag of aquifers is decisive in the measures effectiveness. By means of nitrogen cycle simulation in the river basin district and with the help of the monthly distributed PATRICAL model, the Júcar RBA has defined the measures to be applied and the exemptions to reach the objectives in GW in relation to nitrate pollution. Both, model and methodology are useful for other river basins to define measures.

The total nitrogen inputs in the Júcar RBD amounts to 180,000 tN/year, which represents a nitrogen surplus of 80,000 tN/year and a pressure of 58.5 kgN/year/ha-crop. Around 3/4 of GW bodies have currently the good status while the remaining of GW bodies could reach the good status during following hydrological planning cycles through the implementation of modernized irrigation systems that include fertigation - the use of fertilizers in the water for irrigation-. The implementation of this scenario involves increasing efficiency in fertilizer application, in order to reduce nitrogen losses from slightly under a half to less than 1/3.

## 1. Introduction

Water pollution by nitrate produces negative impacts on human and environmental health (Rios et al., 2013). Exposure to higher concentrations of nitrates or nitrites has been associated with increased incidence of stomach and gastric cancer in adults, and possible increased incidence of brain tumours, leukaemia, and nasopharyngeal (nose and throat) tumours in children (USEPA, 2007). Also, the main health effect for children is the “blue baby syndrome” (methemoglobinemia), seen most often in infants exposed to nitrate from drinking water (USEPA, 2007). In aquatic ecosystems, elevated concentrations of nitrate can help to produce eutrophication.

The global increase in nitrogen (N) use as chemical fertilizer (Heffer, 2012) or as organic input from large livestock population, produced a general increase of nitrate concentration in surface water (SW) (Aquilina et al., 2012) and groundwater (GW), which, in recent decades, has become a major environmental concern (Galloway et al., 2004; Vitousek et al., 1997). Many regions have significantly altered the global nutrient cycle (Ferrant et al., 2011), such as the following: Upper Mississippi River (Houser and Richardson, 2010), Northeastern United States (Howarth et al., 1996; Berka et al., 2001; Boyer et al., 2002), New Zealand (Gillingham and Thorrold, 2000; Monaghan et al., 2005), Ireland (Neill, 1989; Watson and Foy, 2001), United Kingdom (Webb and Walling, 1985; Reynolds and Edwards, 1995; Whitehead et al., 2002b), Norway (Blecken and Bakken, 1997), France (Ruiz et al., 2002; Molenat et al., 2002; Martin et al., 2004) and Portugal (Pacheco and Sanches-Fernandes, 2016). Specially, nitrate concentration reaches higher values in GW, thus there are great extensions of GW polluted by nitrate in the world: in the USA, Canada, Japan, Europe and Australia (Deng et al., 2011), and also northeast China (Huan et al., 2012) and Yellow River (Shen et al., 2011).

The US Protection Agency (US EPA) has established a maximum contaminant concentration of 10 mg/L  $\text{NO}_3\text{-N}$  (USEPA, 2000) or 45 mg/L  $\text{NO}_3$  for drinking water while the maximum acceptable concentration of nitrate for potable water according to the World Health Organization (WHO), is 50 mg/L  $\text{NO}_3$  or 11.3 mg/L  $\text{NO}_3\text{-N}$ . The purpose of both the EU Nitrates Directive (EC, 1991) and the Groundwater Directive - GWD- (EC, 2006), according with the Water Framework Directive -WFD- (EC, 2000),

is to keep nitrate concentration in GW below a threshold of 50 mg/L. Once a water source is contaminated, the costs of protecting consumers from nitrate exposure can be significant. Nitrate cannot be removed by conventional drinking water treatment processes; its removal requires additional, relatively expensive treatment units (USEPA, 2004).

Due to the long time-lag in the groundwater system, it could take decades for leached nitrate from the soil to discharge into freshwaters (Wang et al. 2012; Wang et al 2013 and Wang et al 2016). Besides, the intercrop periods were identified as critical periods for nitrate leaching (Dupas et al., 2015) and total annual precipitation and catchment connectivity are important for nitrate-N transport, with fluxes in a wet year roughly doubling that recorded in a dry year (Outram et al., 2016).

Models can help better understand the nitrate pollution in SW and GW in a large river basin. They are needed to understand direct interactions between land cover and water pollution by nutrient in space and time (Ferrant et al, 2011), and also, to assess the effectiveness of the implementation of programmes of measures.

Models are widely used to simulate N cycle and N transport at plot scale or small catchment scale (Brisson et al., 1998; Vanclooster et al., 1995) and to determine the nitrate concentration in river and the N-exportation rates (Ferrant et al., 2011; Zhang et al., 2016). Large-scale catchments have been modelled by integrating GIS or decision support modules (Lake et al., 2003; Lasserre et al., 1999; Lunn et al., 1996) and it has been suggested that the appropriate use of these different model types will depend on the scale of investigation (Quinn, 2004). Moreover, in most of these models, the GW compartment has a limited role and may even be lacking in GIS or statistical models (Aquilina et al., 2012); thus, in studies of GW at regional scale, it is usual to apply the approach based on the vulnerability assessment, such as the application of the DRASTIC model (Huan et al., 2012; Martínez-Bastida et al., 2010).

In Ferrant et al, (2011) it is indicated that several models (Breurer et al., 2008) have coupled an hydrological model and a crop model to study the interactions between agricultural practices and catchment physical characteristics on the dynamics of N in streams (Mangold and Tsang, 1991; Vachaud et al., 1993; Styczen and Storm, 1995; Lunn et al., 1996; Beaujouan et al., 2002; Whitehead et al., 2002a; Wade et al., 2004;

Liu et al., 2005; Flipo et al., 2007). Also, SW and GW models are coupled to simulate nitrate in GW such as, SWAT-MODFLOW-MT3DMS models to simulate a large aquifer of 11600 km<sup>2</sup> in India (Narula and Gosain, 2012). Hydrogeological models GROWA-DENUZ/WEKU, were coupled to the agro-economic model RAUMIS to define measures to reach the nitrate objective in SW and GW in the Federal State of North Rhine Westphalia in Germany (Kuhr et al, 2015). Lumped-parameters models were developed to simulate future nitrate conditions in the Gaza Coastal Aquifer (Hajhamad and Almasri, 2009) and, also, to determine the best management options to reduce nitrate concentration in GW.

While mitigation programs have been developed to reduce N input to the SW, the effects of such attempts remain relatively limited (Aquilina et al., 2012); there is a consensus that more efforts are required to reduce nitrate concentrations in rivers and aquifers. River Basin Authorities and Nacional/Regional Governments must apply new approaches and strategies to reverse this trend and to recover the status of the aquifers. The Water Framework Directive (WFD) requires no further deterioration as well as a progressive reduction of pollution to reach the good status in the GW bodies in the year 2015. Also, the WFD indicates that in case of specific conditions as for instance technical feasibility, disproportionately expensive or natural conditions -such as long time-lag in the groundwater system which does not allow timely improvement in the status of the water body-, the deadline may be extended (exemptions in following 6-year period, 2021, 2027 ...). The River Basin Management Plan (Annex VII of WFD) must establish the specific nitrate concentration in each GW body for the year 2015 the extended deadlines foreseen and the measures to achieve these nitrate objectives.

In Europe -EU-27-, the averaged pressure (nitrogen surplus) is around 60 kgN/ha of crops (ha-crop) (Leip et al. 2011). Spain has lower nitrogen pressure than the average, around 50 kgN/ha-crop, and much lower than other countries, such as the Netherlands (250-300 kgN/ha-crop), Belgium (150-200 kgN/ha-crop) or Denmark (130-150 kgN/ha-crop). However a large number of aquifers in Spain, mainly in the semiarid areas, are polluted by nitrate. This is produced because the aquifer recharge is minor in the semiarid areas of Spain than in other areas with humid climate, and thus, the same nitrogen pressure (or even minor pressures) over the aquifers, produces higher nitrate

concentrations. For this reason, the Spanish Mediterranean areas are more vulnerable to nitrate pollution than other areas with humid climate.

In this paper, it is described how the Júcar River Basin Management Plan (RBMP) establishes, in a scientific and rigorous manner, the exemptions (mainly deadlines) and measures required to reach the objectives in relation to nitrate pollution in the GW bodies, taking in account the long time-lag of watersheds and aquifers. The methodology presented is common to the entire territory of Spain and it is based on the application of a distributed hydrologic and water quality simulation model, the PATRICAL model. The hydrologic module, its formulation and application to the Júcar River Basin District (RBD), is described in Pérez-Martín et al. (2014), and the nitrate module (formulation and application) is presented here. The methodology has two steps: 1) model calibration to the observed data; 2) nitrate simulation for three future scenarios with different degrees of implementation of mitigation measures. The main contributions of this manuscript are: 1) presents a new nitrate transport model for large river basins that is distributed, parsimonious (reduced number of parameters) and includes SW, GW and their interactions; 2) presents a methodology developed by the Júcar RBA to determine the measures required to recovery aquifers, and the year that it is produced, taking in account the long time-lag of aquifers; 3) the model and the methodology presented is applicable to other river basins in Europe that are currently working in establish the nitrate concentration objectives in the GW bodies and the measures - and deadlines - required to recovery the aquifer status, as evidenced by subsequent application to the entire Spanish territory.

The effect of these three fertilizer application scenarios on nitrate concentrations has been assessed with the simulation model. The scenarios are: 1) baseline scenario, which corresponds to maintaining the current fertilization; 2) optimal scenario, which involves the application of the nitrogen optimal dose and includes the fertilizers in the drip irrigation; this requires a strong economic investment through the application of techniques such as fertigation, which include the use of fertilizers in the drip irrigation; 3) trend reversal and improvement scenario, which is an intermediate stage between the two previous ones and includes the development of the action plans defined in current vulnerable areas; this is the more plausible scenario in the short to medium term.

The PATRICAL model simulates the nitrate cycle in medium/large basins, as it is the case of the entire Spanish territory (500,000 km<sup>2</sup>) where it is applied (Pérez-Martín et al. 2012). The model uses the water flows and water storages obtained by its hydrological module in altered conditions by human activities. The model obtains the monthly nitrate concentrations in aquifers and surface flows. This model has only three parameters to simulate the nitrate transport in the entire river basin, thus it can be stated that the model is very parsimonious. The results obtained with this methodology are: the GW bodies that are foreseen to reach the objective in the year 2015 (nitrate concentration lower than 50 mgNO<sub>3</sub>/L) and the GW bodies that require extended deadline until next water planning cycles: 2021, 2027, 2033 or 2039. Also, other valuable results are the definition of the measures needed to reach these objectives in each GW body.



## 2. Methods and Data Sets

### 2.1. The Simulation Model

The PATRICAL model is a large-scale (medium/large RBs), conceptual, monthly and spatially distributed (grid  $1 \times 1 \text{ km}^2$ ) water balance and water quality model (for multi-decadal periods 50–100 years). The description of the hydrological model -components, water storages and fluxes and hydrological parameters- and its calibration and application to the Júcar RBD- is addressed in Pérez-Martin et al. (2014). The nitrate module has three storages in each cell (i.e.  $1 \times 1 \text{ km}$ ), (Fig 1c): 1) Soil Storage, where nitrogen is included in the soil moisture. 2) Unsaturated Zone, between the root zone and the GW level. 3) Aquifer, which corresponds with the saturated zone, where a complete mixing of substances in water is considered. The model has the following modules (Fig. 1c and formulation in the Appendix): 1) Nitrogen balance on soil, 2) Nitrogen balance on unsaturated zone, 3) Nitrogen balance in the aquifer, 4) Routing Module and River Losses, and 5) Groundwater Transfer Module.

In this model, point source (PS) and non-point source (NPS) pollution are incorporated. PS pollution comes mainly from wastewater treatment plants from urban and industrial areas and it is transported directly by surface runoff. NPS pollution - nitrogen surplus (Fig. 1a)-, comes mainly from fertilizers, manures and deposition. NPS pollution is located in soil and is carried by water, as nitrate, by surface runoff and infiltration into the aquifer (Fig. 1b).

The nitrogen surplus is retained in soil (Fig. 1c), where volatilization and the water transport is produced. Nitrate is carried by surface runoff to the rivers and by infiltration to the unsaturated zone. Nitrate is retained in the unsaturated zone, where the amount retained depends on the unsaturated thickness, which is the difference between surface and the monthly simulated GW level. The nitrate in the unsaturated zone is washed out by deeper infiltration into the aquifer. The aquifer is considered as an aggregate element and GW discharges represent the nitrate outputs of the aquifer. Nitrate from surface runoff and GW discharges, is routed into the river. Finally, nitrate transported by transfers between groundwater bodies and river losses, is computed.

Only three parameters with a unique value for the entire basin are defined in the model: 1) de-nitrification constant for a long stay of nitrate in soil ( $k_{den}$ , dimensionless  $[0, \infty]$ ), which defines the volatilization rate of the nitrogen stored in soil; 2) nitrate transfer coefficient in soil ( $k_s$ , dimensionless  $[0, \infty]$ ), which determines the facility of water to wash out the nitrate from soil and thus the amount of nitrate retained in soil; and 3) nitrate transfer coefficient in the unsaturated zone ( $k_{uz}$ ,  $\text{mm}^{-1}$   $[0, \infty]$ ), which represents the facility of water to wash the nitrate from the unsaturated zone.

The sensibility analysis shows that high values of  $k_{den}$  ( $> 5$ ) imply that all the nitrogen will be volatilized in the next month, while the 0 value implies that there is no nitrogen volatilization. Low values of  $k_s$  increase the amount of nitrogen retained in soil while high values ( $> 3$ ) produce a rapid wash of nitrate from soil. Low values of  $k_{uz}$  mean that the nitrogen needs a long time to reach the aquifer, high values ( $> 1$ ) imply that all the nitrogen reach the aquifer in less than a year.

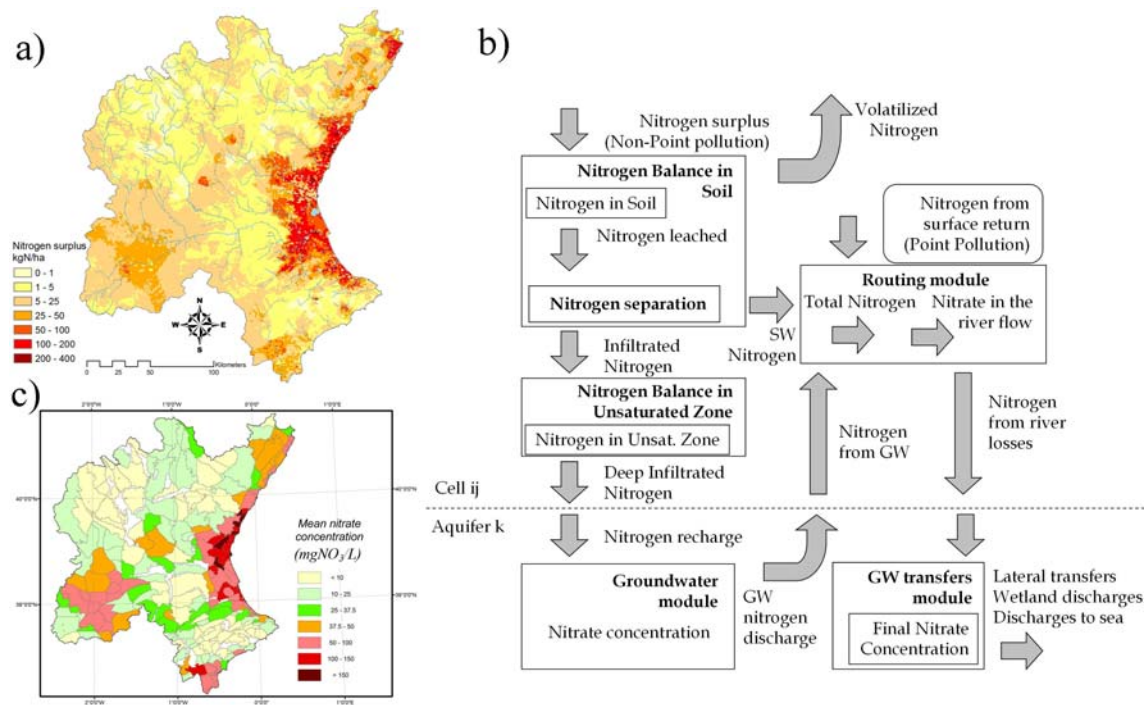


Fig. 1. a) Distributed nitrogen surplus (kgN/ha) and b) simulated nitrate concentration in groundwater (mgNO<sub>3</sub>/L) and c) structure and variables of the nitrate module of PATRICAL model.

## 2.2. The Júcar River Basin District

The Júcar River Basin District (RBD) (43,000 km<sup>2</sup>) is located on the Mediterranean side of the Iberian Peninsula (Fig. 2a). In the Júcar RBD, there are 90 GW bodies defined. A GW body is formed by one or more aquifers, and it is an administrative delimitation of GW. In the model, a GW body can be divided in various sectors, corresponding to the aquifers delimitation or to the different behaviour detected in different parts of the GW body. The model includes the simulation of more than 200 sectors in this river basin (Fig. 2b). A further description of the Júcar RBD is included in Ferrer et al. (2012) and Pérez-Martín et al. (2014).

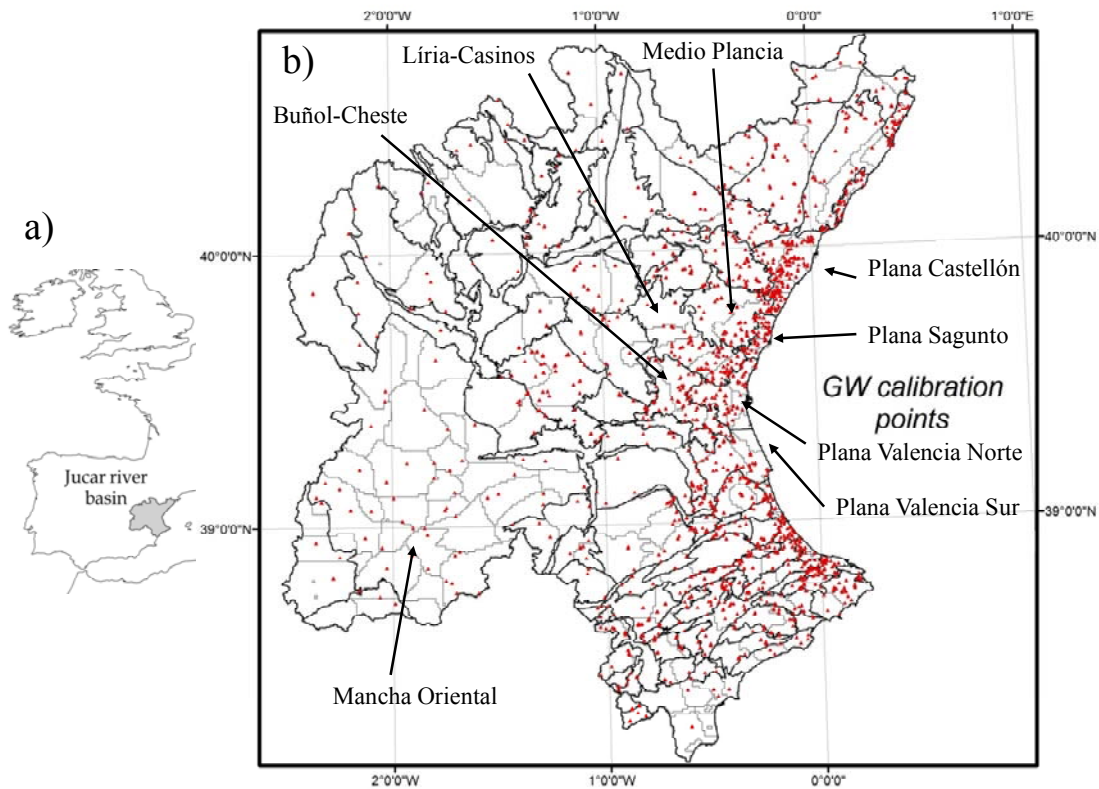


Fig. 2. a) Júcar RBD location b) GW and Sector delimitation and nitrate GW network.

Nitrogen surplus comes from the annual balance of nitrogen in soil at municipal level for the period between the years 2000 and 2011 (MARM, 2014). The mean balance in the Júcar RBD for the period 2007-2011 (Table 1) shows that 80% of inputs comes from inorganic/organic fertilizers (57/13%) and atmospheric deposition (10%), while harvest (crops and woods) and volatilization represents nearly 90% of the outputs.

Inorganic fertilizers are the major input of nitrogen in the river basin, representing 57% thereof. Atmospheric deposition is associated to the atmospheric volatilization produced in the nearest area, so it also depends on the total nitrogen input produced in the nearest area.

The NPS pollution, i.e. the nitrogen surplus, is around 80,000 t of Nitrogen per year (tN/year) and it represents 44% of the total nitrogen inputs (181,000 tN in Table 1), which produces a mean pressure of 58.5 kgN/ha-crop. The global pressure related to the entire extension of the Júcar RBD is 18.5 kgN/ha.

Inputs	tN	rel	kgN/ha-crop	Outputs	tN	rel	kgN/ha-crop
Inorganic Fertilizers	103,060	0.57	75.9	Crop Harvest	58,856	0.58	43.3
Organic Fertilizers	23,932	0.13	17.6	Wood Harvest	15,380	0.15	11.3
Atmospheric Deposition	18,766	0.10	13.8	Stubble Burning	6,235	0.06	4.6
Nitrogen from Urban Waste	12,769	0.07	9.4	Pasturages	1,750	0.02	1.3
Nitrogen in Water	8,341	0.05	6.1	Fertilizers Volatilization	16,794	0.16	12.4
Livestock Manures	7,715	0.04	5.7	Pasturages Volatilization	1,421	0.01	1.0
Biological Fixation	5,202	0.03	3.8	Fertilizers Denitrification	1,119	0.01	0.8
Seeds	1,563	0.01	1.2	Others Denitrification	212	0.00	0.2
				Pasturages Denitrification	114	0.00	0.1
<b>TOTAL</b>	<b>181,348</b>	<b>1.00</b>	<b>133.5</b>	<b>TOTAL</b>	<b>101.879</b>	<b>1.00</b>	<b>75.0</b>
<b>Surplus</b>					<b>79.469</b>	<b>0.44</b>	<b>58.5</b>

Table 1. Averaged 5-year nitrogen balance in soil in the Júcar RBD for the period 2007-2011.

Nitrogen surplus at municipal level are spatially distributed within the municipality by means of the land use map (Corine Land Cover: CLC, 2000). Higher values are located mainly inside major agricultural areas (Fig. 1a) such as near the Mediterranean Sea (50 - 200 kgN/ha) and the Eastern Mancha Aquifer (25 kgN/ha).

### 2.3. Model Calibration and Validation

The model runs from October 1970 until September 2012 and it requires hydro-meteorological data, described in Pérez-Martín et al. (2014), and the nitrogen surplus data generated in the river basin. The nitrogen surplus data comes from the municipal nitrogen balance (described in section 2.1) for the period 2000-2011, and for the rest of the simulation period corresponding to previous years (1970-1999), nitrogen surplus is obtained combining the municipal balance (2000-2005) with the evolution of the global nitrogen use in Spain from 1970 to 2005.

The model is calibrated with nitrate data from GW network and it is validated with the GW bodies status evaluation made by the Júcar RBMP (CHJ, 2015). There is a large amount of available data: 7658 samples, from January 2000 to October 2013, distributed in 1874 GW gauging stations in the Júcar RBD (Fig. 2b). The average number of data by station is 4, less than 200 stations have more than 10 available data, and only 4 stations have more than 20 available samples. The large amount of available data allows determining with a great deal of certainty, the current status of the GW bodies. However, there is a reduced number of check points with insufficient data to determine historical trends or the variability of the processes involved.

Model performance was assessed using a double criteria approach: 1) a visual inspection of the model results in all the aquifers modelled with the observed data (some examples in Fig. 3), and 2) fitting the average nitrate concentration simulated in last years (oct-2005 to sep-2013) in each aquifer, to the mean nitrate concentration of the all samples available in each aquifer in the same period (Fig. 5). The fitted values of the parameters for the entire watershed are:  $k_{den}$  (dimensionless) = 0.05,  $k_s$  (dimensionless) = 3.0 and  $k_{uz}$  ( $\text{mm}^{-1}$ ) = 10.0. Only three numerical values determine the nitrate behaviour in the entire river basin, so this provides a great robustness to the model.

Nitrate concentrations over the last years are stabilized in all the aquifers. The model results are included in the range of the observed data in different points of the aquifers (3 observed points in Fig. 3.). There are high differences between data observed in

different points of the same aquifer (Fig. 3a and Fig. 3f) and also between different samples of the same point (obs. 1 in Fig. 3a and obs. 3 in Fig 3e).

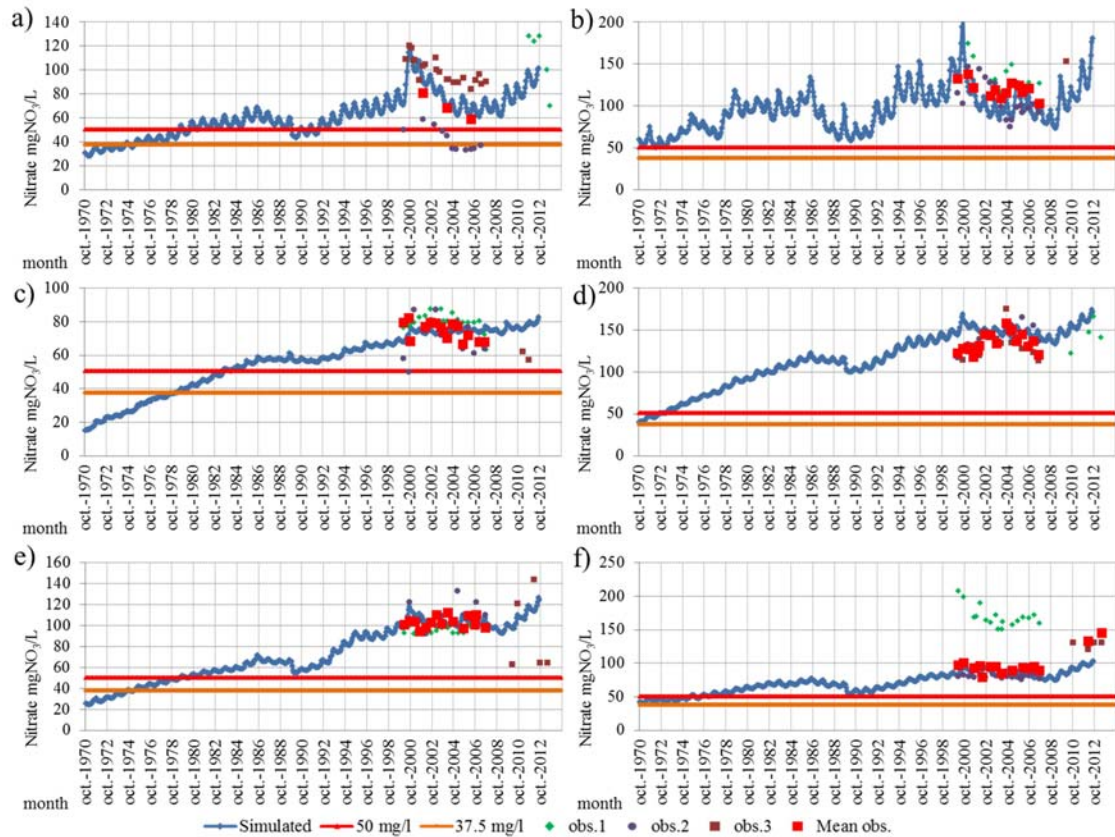


Fig. 3. Nitrate concentration (mgNO<sub>3</sub>/L) simulated and observed, including data of 3 observed points in the aquifer and the mean values of the all observed data, in different aquifers in the Júcar RBD: a) Plana de Castellón, b) Plana de Sagunto, c) Medio Palancia, d) Liria-casinos, e) Plana de Valencia Norte and f) Plana de Valencia Sur.

A multi-year variability in nitrate concentrations is detected in model results, which is also confirmed with the observed data of Plana de Castellon and Plana de Sagunto (Fig 3a and b). In both cases, observed nitrate concentrations decreased from 110 and 200mgNO<sub>3</sub>/L respectively in fall of 2000, to 70 and 100 mgNO<sub>3</sub>/L in summer of 2006. In the model, the multi-year variability depends on the annual amount of water that infiltrates into the aquifer and the unsaturated zone thickness. The aquifer Medio Palancia (Fig. 3c) has the major thickness (around 100 m) of the cases presented, so nitrate concentrations -around 80 mgNO<sub>3</sub>/L- have more long time-lag than the rest of cases (thickness around 30 m, Fig. 3).

A strong convective rainfall was produced near the coast in October 2000. This rainfall carried a large amount of nitrate from soil and the unsaturated zone to the aquifers, so nitrate concentration strongly rose in this month in the aquifers. Over the next months/years the nitrate concentration in the aquifers will be declining, because soil and unsaturated zone (without nitrogen) is retaining the new nitrogen applied in the river basin.

The years 1989, 1990 and 1991 were three consecutive very wet years (Fig. 4a). During this period the model simulates a reduction in nitrate concentration in the aquifers (no observed data is available in this period). Similarly during the dry periods (1980-1987, 1992-1999 and 2009-2011) the descending stretches of standardized accumulated monthly deviation recharge observed in Fig. 4b) are associated to increases in the nitrate concentration (Fig. 3).

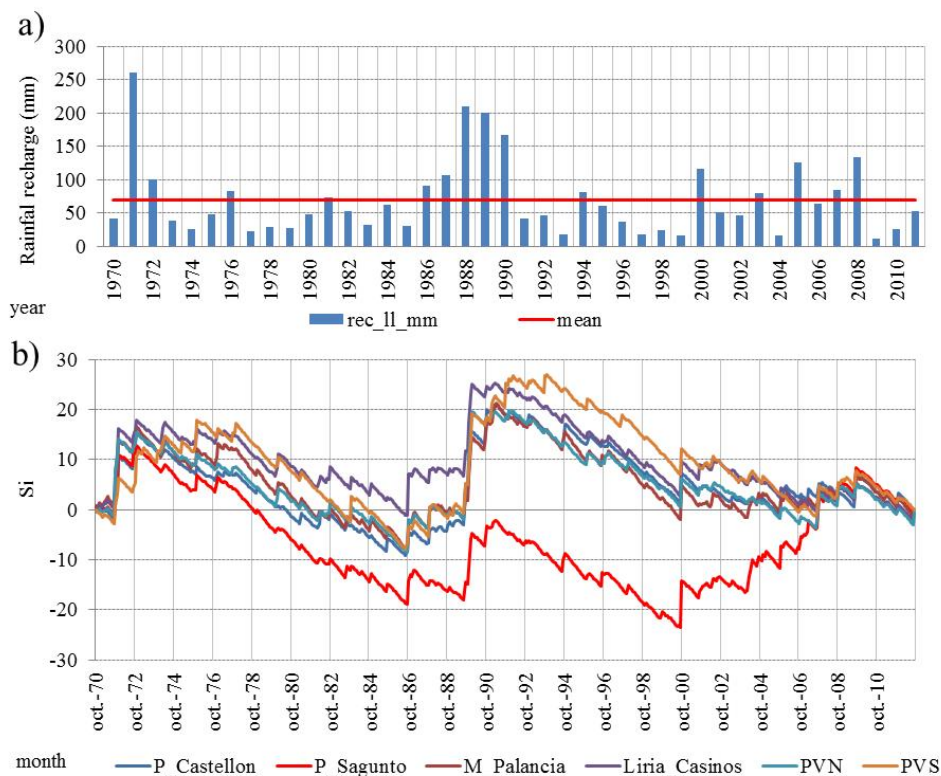


Fig. 4. a) Annual rainfall recharge (mm) near the coast in the Júcar RBD and b) standardized accumulated monthly deviation recharge (dimensionless).

Model is also calibrated fitting the average nitrate concentration simulated in the years (oct-2005 to sep-2013) in each aquifer to the mean nitrate concentration of all the



samples available in each aquifer in the same period (fully mixed hypothesis are used to simulate the nitrate behaviour in the aquifers). Moriasi et al. (2007) indicates that in general, model simulation can be judged as satisfactory if Nash-Sutcliffe efficiency (NSE)  $>0.50$  and if percent bias (PBIAS)  $\pm 25\%$  for streamflow, PBIAS  $\pm 55\%$  for sediment, and PBIAS  $\pm 70\%$  for N and P. In this work, the NSE cannot be evaluated adequately due to the reduced number of available data along the time in the same point, so only the PBIAS is used to judge the model performance. In this case, the model has a very good performance (PBIAS  $\pm 25\%$ ) in 27% of the aquifers, good or very good performance (PBIAS  $\pm 40\%$ ) in 73% of the aquifers, satisfactory (or better) performance (PBIAS  $\pm 70\%$ ) in 88% of the aquifers and unsatisfactory performance in 12% of the aquifers. The correlation coefficient between average simulated and average observed data in each aquifer is  $R=0.84$  (Fig. 5). As regards to aquifers with higher nitrate concentration, observed data greater than 50 mgNO<sub>3</sub>/L or close to that value ( $>35$  mgNO<sub>3</sub>/L), show a correlation coefficient between observed and simulated values of  $R=0.63$ .

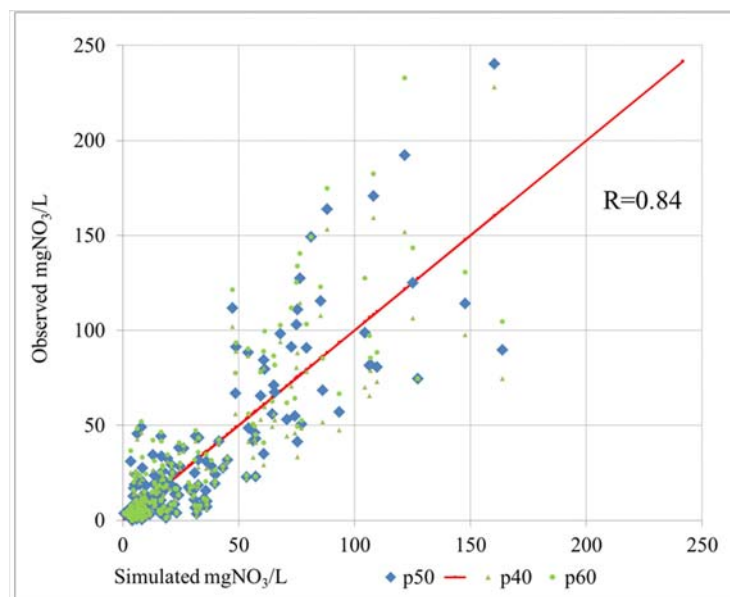


Fig. 5. Mean nitrate concentration (mgNO<sub>3</sub>/L) observed (and percentiles 40 and 60 -p40, p60) and simulated in each aquifer.

Model results validation of the 90 GW bodies was made with the chemical status assessment made by the Júcar RBMP (CHJ, 2015). This official assessment is made according to the criteria established in the GWD (EC, 2006), and is based on the



chemical GW network, assuming a representative weight to each control point located in the same GW body. High nitrate concentrations are located in areas near the coast and in the Mancha Oriental Aquifer (Fig. 6a); these areas are officially assessed in Not-Good status by the Júcar RBMP (Fig. 6b). Minor discrepancies are found between model results and the official assessment. These discrepancies are located in four GW bodies without intensive agriculture and low nitrogen pressure (Fig. 6b) and a detailed analysis is developed in these four GW bodies. In three of them -“Javalambre Occidental”, “Lezuza-El Jardín” and “Arco de Alcaraz”- the GW network is clearly not representative of the GW body global behaviour. Finally, there is only one case, “Almansa” GW body, wherein it is not clear if discrepancy is related to model limitations or rather to the lack of representativeness of the observed data. The great concordance between chemical status and model results, and also, the detailed analysis that justifies those discrepancies are mainly due to the lack of representativeness of the data network and indicates the great robustness and reliability of the proposed model.

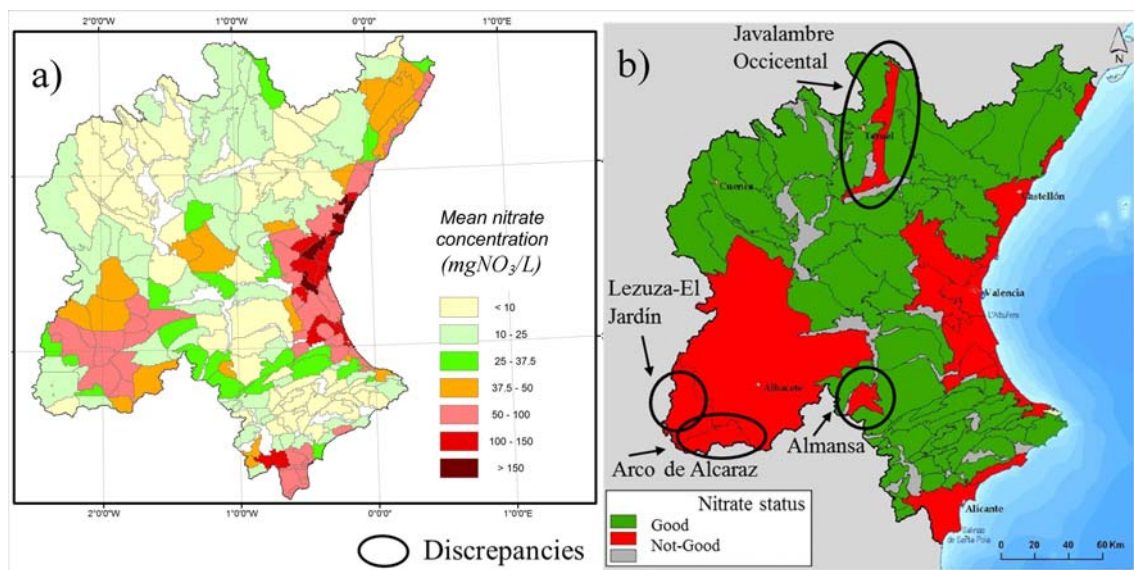


Fig. 6. a) Simulated mean nitrate concentration (mgNO<sub>3</sub>/L) in GW for the period 2010-2012. b) Nitrate status in the Júcar RBMP (Júcar, 2015).

Model results indicate that 26% of the annual averaged nitrogen surplus (79,469 tN/year) is volatilized from soil during the year (20,500 tN/year), additional to the 18,215 tN/year volatilized during the nitrogen application. A large amount of nitrogen (38,719 tN/year) is emitted to the atmosphere (21% of the total nitrogen input – 181,348

tN/year). Shcherbak et al. (2014) indicates that Nitrous oxide (N<sub>2</sub>O) is a potent greenhouse gas (GHG) that also depletes stratospheric ozone and that Nitrogen (N) fertilizer rate is the best single predictor of N<sub>2</sub>O emissions from agricultural soils, which are responsible for ~50% of the total global anthropogenic flux, although it is a relatively imprecise estimator. Turner et al., 2015, indicates that N<sub>2</sub>O deleterious effects on the environment have prompted appeals to regulate emissions from agriculture, which represents the primary anthropogenic source in the global N<sub>2</sub>O budget.

74% of the nitrogen surplus is carried by water (58,965 tN/year), 31% of this (18,193 tN/year) by surface runoff and gets into the rivers. Finally, the remaining part (69%, 40,772 tN/year) is carried by infiltration and reaches the aquifers. In the Júcar RBD, the average amount of nitrogen in soil is 8 kgN/ha and the average value in the unsaturated zone is 5 kgN/ha. In the intensive agricultural areas the amount of nitrogen in soil mainly ranges from 20 to 40 kgN/ha.

### 3. Future Groundwater Nitrate Concentration

The nitrate concentration in each GW body and the measures needed to achieve the objective, are determined by simulating three future scenarios, from 2015 to 2039 to cover four water planning cycles (each water planning cycle in EU countries has 6 years). The scenarios are characterized by the doses of fertilization applied, as follows: 1) Baseline scenario: the nitrogen applied in the future is the same as last years (2008-2011), 2) Optimal scenario: the nitrogen applied corresponds to plants requirements (optimal doses); though , this scenario could imply a nitrogen deficit in the plant if the irrigation systems have not been modernized and 3) Trend Reversal and Improve (TR&I) scenario: this is an intermediate scenario between previous scenarios.

The mean pressure in the Júcar RBD (table 2) varies between 18.5 kgN/ha (58.5 kgN/ha-crop) in the baseline scenario, to 10.4 kgN/ha (32.9 kgN/ha-crop) in the optimal scenario, placing the investment scenario in an intermediate case with 14.4 kgN/ha. The optimal scenario includes a nitrogen reduction of 35,890 tN/year (20% reduction in the total inputs), which is produced basically with a minor application of mineral fertilizers of 26,600 tN/year (reduction of 26% in the fertilizers application) and the subsequent minor atmospheric deposition of 2,650 tN/year (reduction of 14% in the atmospheric deposition). This reduction in the application of mineral fertilizers (26%) produces a significant reduction in the nitrogen surplus of 44%.

The implementation of the optimal scenario requires the modernization of the traditional irrigation systems, including the fertigation as the main measure to reduce nitrogen application in crops. This measure requires a large investment to modernize these irrigation systems. The Júcar River Basin Management Plan (RBMP) and the Programme of Measures (CHJ, 2015) includes the modernization of irrigation (drip irrigation) as one of the major measures to be applied in this Mediterranean area (area with water scarcity), aiming to achieve water savings and also other environmental objectives, such as reducing the use of fertilizers. The Júcar RBMP includes a government investment of 431 million euros between 2015 and 2027.

Scenario	Baseline	TR&I	Optimal
Nitrogen inputs (tN/year) (a)	181,348	163,389	145,430
Nitrogen outputs (tN/year)	101,879	101,292	100,705
Nitrogen surplus (tN/year) (b)	79,469	62,097	44,725
Relative surplus (b/a)	0.44	0.38	0.31
Local Nitrogen pressure (kgN/year/ha-crop)	58.5	45.7	32.9
Local Nitrogen pressure (kgN/year/ha of crops and pastures)	32.1	25.1	14.4
General Nitrogen pressure (kgN/year/ha Júcar RBD)	18.5	14.4	10.4

Table 2. Characterization of future nitrogen scenarios.

The long time-lag in GW implies a large period of time to achieve the objective after the application of measures. This long time-lag is different in each aquifer, and mainly depends on the following: the aquifer extension, the aquifer hydrogeological characteristics, the thickness of the unsaturated zone and the water fluxes produced in the aquifer.

In the case of Buñol-Cheste GW body (Fig. 7), the nitrate concentration is stabilized around 100 mgNO<sub>3</sub>/L under the baseline scenario and no recovery is produced. Under TR&I scenario the trend is changed and a weak recovery is produced. Finally, only with the implementation of the optimal scenario the objective is reached; though around 25 years are required to reach this objective.

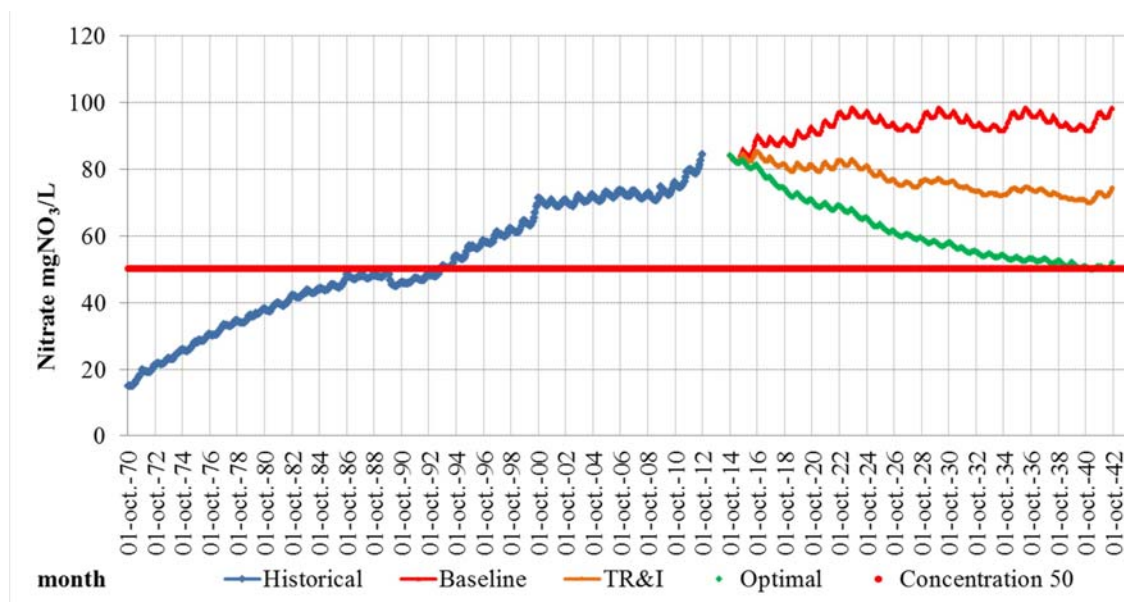


Fig. 7. Simulated mean nitrate concentration (mgNO<sub>3</sub>/L) for the historical period 1970-2011 and the three future scenarios in the Buñol-Cheste GW body.

74% of GW bodies (67 of 90) reach the objective (nitrate concentration below 50 mgNO<sub>3</sub>/L) in the year 2015 (Table 3). Four of these require the application of optimal doses of fertilizer to maintain the objective. The intensive irrigation areas of the Júcar RBD, coastal aquifers and Mancha Oriental aquifer, are the areas where the aquifers (23 out of 90) do not reach the objective in the year 2015 (Fig. 8a). In these areas the optimal scenario is required to achieve the objective the following cycles of 6 years (Fig. 8b). Besides, in four GW bodies additional measures (well as the application of optimal doses) are needed to reach the objective in the year 2039.

Year to reach	Number GW bodies	ratio	Baseline	TR&I	Optimal	Additional
2015	67	74%	62	0	5	0
2021	6	7%	1	4	1	0
2027	9	10%	0	0	9	0
2033	2	2%	0	0	2	0
2039	6	7%	0	0	2	4
<b>Total GW bodies</b>	<b>90</b>	<b>100%</b>	<b>63</b>	<b>4</b>	<b>19</b>	<b>4</b>

Table 3. Number of GW bodies that reach the objective in each water planning cycle and measures required to accomplish it.

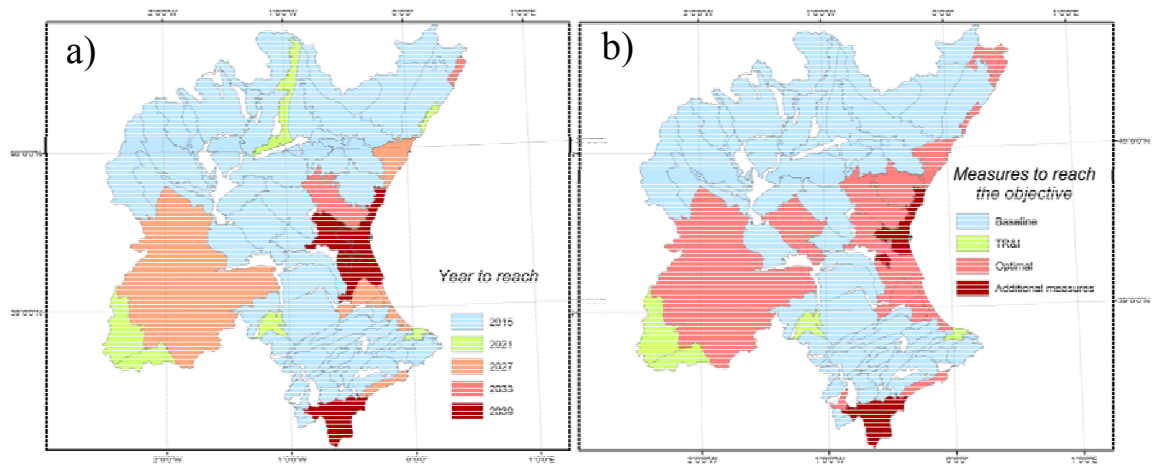


Fig. 8. a) Year to reach the environmental objectives in each GW body and b) measures required to achieve the objective in each GW body.

#### 4. Conclusions

This paper shows how to establish, the exemptions to achieve the nitrate objectives in the groundwater (GW) bodies in a large river basin district according to the EU Water Framework Directive (WFD) and the measures to be applied to reach these objectives. The methodology presented is based on the use of the PATRICAL model that simulates the nitrogen cycle for a long period of time. The model and the methodology presented in this work is applicable to other river basins in the World and mainly in Europe, as it is demonstrated by the currently application to the entire Spanish territory.

The parameters are calibrated by fitting model results in each aquifer to the observed time series and, also, by fitting current average results to mean concentration in each aquifer. The model shows a satisfactory performance in 88% of the aquifers modelled that have high nitrate concentrations, and a good performance in 73% of the aquifers. Model results are validated with the official status assessment of the GW bodies made by the Júcar RBMP, where no significant discrepancies have been found. The nitrate model is quite robust because with only three parameters with the same value in the entire river basin, it fits the behaviour of aquifers in the entire river basin.

In the Júcar RBD, current nitrate concentration in GW reaches values higher than 50 mgNO<sub>3</sub>/L, in a large number of GW bodies (23 of 90). The areas which currently have high values are the following: the coastal aquifers, where in some areas it reaches concentrations of 100-150 mg/L, and the Mancha Oriental aquifer, where in some specific areas the nitrate concentration is higher than 50 mgNO<sub>3</sub>/L. In general terms, currently the nitrate concentration in GW has stabilized, with no trend; only a few deep aquifers, due to their major long time-lag, show some upward trend such as Medio Palancia or Buñol-Cheste aquifer.

The horizons in which nitrate WFD objectives are reached in each GW body and the measures needed to do it were determined by simulating three future scenarios from the year 2015 to 2039, covering four water planning cycles of 6 years. The implementation of modernized irrigation systems, including the fertigation systems to apply the fertilizers, could reduce the use of fertilizers and allows to meet the WFD objectives in the following planning cycles. The reduction in the application of mineral fertilizers (26% optimal scenario) produces a significant reduction in the nitrogen surplus (44%

optimal scenario). Based on the 23 GW bodies that do not currently meet the objectives, 15 of them could achieve the objective before the year 2027 and the rest before the year 2039. The more or less prolonged period of time required to comply with the objectives, depends on the long time-lag of each aquifer.

## Acknowledgements

The authors would like to sincerely thank the Júcar River Basin Authority, Confederación Hidrográfica del Júcar, for providing data and using the model.

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## Appendix. Model formulation

Summary of model variables is included in Table A1 and model parameters description is included in Table A1

<Table A1>

### 1. Nitrogen Balance in Soil

Nitrogen in soil  $N_{soil_{ij,t}}$  (kgN/ha), in cell "ij" in month "t", is obtained by mass balance.

$$N_{soil_{ij,t}} = \left( N_{soil_{ij,t-1}} + N_{sur_{ij,t}} - N_{leach_{ij,t}} \right) \cdot e^{-k_{den}} \quad (A1)$$

$N_{soil_{ij,t-1}}$  is the amount of nitrate in soil from previous month,  $N_{sur_{ij,t}}$  (kgN/ha) is the nitrogen surplus generated in this month,  $k_{den}$  is the denitrification constant and  $N_{leach_{ij,t}}$  (kgN/ha) is the nitrogen leached from soil, which is computed by:

$$N_{leach_{ij,t}} = \left( N_{soil_{ij,t-1}} + N_{sur_{ij,t}} \right) \cdot \left( 1 - e^{\left( -k_s \cdot \frac{(Wa^*_{ij,t})}{Sw_{max_{ij}}} \right)} \right) \quad (A2)$$

Where:  $k_s$  is the nitrate transfer coefficient of soil,  $Sw_{max_{ij}}$  is the water soil storage capacity (mm),  $Wa^*_{ij,t}$  is the hydrological surplus (mm) corresponding to the sum of surface runoff, infiltration and water returns from irrigation excess.

The nitrogen is leached from soil by the surface runoff (mm)  $R_{sup_{ij,t}}$ , as superficial nitrogen  $N_{sup_{ij,t}}$  (kgN/ha), and the infiltration (mm)  $R_{inf_{ij,t}}$ , as infiltrate nitrogen  $N_{inf_{ij,t}}$  (kgN/ha), both with the same nitrate concentration:

$$N_{sup_{ij,t}} = N_{leach_{ij,t}} \cdot \frac{R_{sup_{ij,t}}}{Wa^*_{ij,t}} \quad (A3)$$

$$N_{inf_{ij,t}} = N_{leach_{ij,t}} \cdot \frac{R_{inf_{ij,t}}}{Wa^*_{ij,t}} \quad (A4)$$

## 2. Nitrogen Balance in the Unsaturated Zone

Infiltrated nitrogen reaches the unsaturated zone, where it is stored  $Nuz_{ij,t}$  (kgN/ha). The balance of nitrate stored in the unsaturated zone has the following expression:

$$Nuz_{ij,t} = Nuz_{ij,t-1} + Ninf_{ij,t} - Nuzinf_{ij,t} \quad (A5)$$

A part of nitrate stored is washed by infiltration and reaches to the aquifer  $Nuzinf_{ij,t}$  (kgN/ha), it is computed as follows:

$$Nuzinf_{ij,t} = (Nuz_{ij,t-1} + Ninf_{ij,t}) \cdot \left( 1 - e^{\left( -kuz \cdot \frac{Rinf_{ij,t} \cdot Imax_{ij}}{d_{ij,t} + 1} \right)} \right) \quad (A6)$$

Where:  $kuz$  is the nitrate transfer coefficient in the unsaturated zone ( $\text{mm}^{-1}$ ),  $Imax_{ij}$  is the monthly infiltration capacity (mm),  $d_{ij,t}$  is the depth of water table (mm).

## 3. Nitrogen Balance in the Aquifer

The aquifer is considered like a dispersive storage, so the nitrogen is totally mixed with the water stored. Nitrate concentration in the aquifer  $CNaq_{k,t}$  is obtained by:

$$CNaq_{k,t} = 4.43 \cdot \frac{Naq_{k,t-1} + NaqI_{k,t}}{Waq_{k,t-1} + Rn_{k,t}} \quad (A7)$$

Where previous nitrogen is obtained by:

$$Naq_{k,t-1} = CNfaq_{k,t-1} \cdot Waq_{k,t-1} \quad (A8)$$

and the nitrogen that reaches the aquifer  $NaqI_{k,t}$  is the sum of the distributed nitrogen above the aquifer,

$$NaqI_{k,t} = \sum_{\text{aquifer}_k}^{i,j} Nuzinf_{ij,t} \quad (A9)$$

Distributed nitrogen discharges to the river  $NaqOd_{ij,t}$  is obtained by:

$$NaqOd_{ij,t} = \frac{1}{4.43} \cdot CNaq_{k,t} \cdot Rsub_{ij,t} \quad (A10)$$

#### 4. Routing Module and River Losses

Nitrogen from aquifers is joined to nitrogen carried by surface runoff  $Nsup_{ij,t}$  and the point pollution discharges  $Ndisch_{ij,t}$ , which together become the total content of nitrate in the surface network.

$$Ntotal_{ij,t} = NaqOd_{ij,t} + Nsup_{ij,t} + Ndisch_{ij,t} \quad (A11)$$

The total nitrate is accumulated in the drainage network  $Nnet'_{ij,t}$  using the digital elevation model (DEM). Monthly nitrate concentration in the river  $CNnet'_{ij,t}$  (mg  $NO_3^-$  /L) is obtained dividing the nitrate accumulation and river flows  $RTnet'_{ij,t}$ .

$$CNnet'_{ij,t} = 4.43 \cdot \frac{Nnet'_{ij,t}}{RTnet'_{ij,t}} \quad (A12)$$

Nitrogen infiltrated from rives is obtained by:

$$NL_{ij,t} = \frac{1}{4.43} CNnet'_{ij,t} \cdot RL_{ij,t} \quad (A13)$$

#### 5. Groundwater Transfer Module

Final nitrate concentration in the aquifer  $k$ ,  $CNfaq_{k,t}$ , is the relation between total nitrogen inputs and total available water, as follows:

$$CNfaq_{k,t} = 4.43 \cdot \frac{Waq_{k,t} \cdot CNaq_{k,t} + NaqRL_{k,t} + \sum_{r=1}^n Fl_{rk,t} \cdot CNaq_{r,t}}{Waq_{k,t} + RLaq_{k,t} + \sum_{r=1}^n Fl_{rk,t}} \quad (A14)$$

Where,  $NaqRL_{k,t}$  is the total nitrogen infiltrated into the aquifer by the river losses  $RLaq_{k,t}$ ,  $Fl_{rk,t}$  is the lateral flows between all the aquifers ( $n$ ) to the aquifer  $k$ .