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Fertigation to recover nitrate-polluted aquifer and improve a long time eutrophicated lake, Spain

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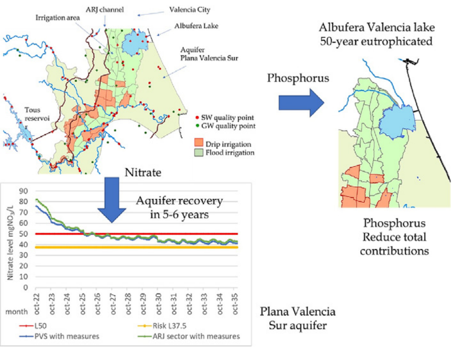
HIGHLIGHTS

- Modernized irrigation system contributes to recover polluted aquifer by nitrates and improves an eutrophicated lake.
- Drip irrigation reduces around 25 % to 45 % nitrogen applied and 70 % and 83 % nitrate leaching.
- Drip irrigation reduces around 90–95 % phosphorus application and eliminates phosphorus contributions to surface waters.
- Applying measures can recover the aquifer in 5–6 years.

GRAPHICAL ABSTRACT



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ABSTRACT

Use of nitrogen and phosphorus in agriculture increases agricultural production but also generates important environmental problems around the world, such as high nitrate levels in aquifers and an increase in eutrophication of waters. A set of tools and models are used, ENVIRO-GRO and PATRICAL models, to analyse the effect of large irrigation system modernization, 13,700 ha, from traditional flood irrigation to modernized drip irrigation, in the aquifer nitrate levels and in the phosphorus inputs to a 50-years eutrophicated RAMSAR lake, Albufera lake.

Based on data collected from end users, modernized irrigation system reduces the amount of nitrogen applied from 25 % to 45 % and phosphorus applied around 90–95 %, so phosphorus content on soil, phosphorus legacy, is reducing by time. Obtained results indicate that nitrogen leaching as nitrate is reduced by 70 % to 83 % and surface runoff during irrigation events disappear, hence phosphorus contributions to surface waters are eliminated. Nitrate polluted aquifer will be recovered in 5–6 years after complete implement of measures and phosphorus inputs to the lake are reduced around 20 % contributing to improve the status of the eutrophicated Albufera lake.

Results show great agreement with the European Strategy to reduce the use of fertilizers and how the fertilizers technical management in fertigation can contribute to greater efficiency in it use and improvement of the environment.

1. Introduction

Nitrogen (N) and phosphorus (P) availability limit plant growth in most terrestrial ecosystems and relative availability of N and P, as reflected by N:P ratios of plant biomass influences vegetation composition and functioning (Güsewell, 2004). Both two main nutrients, N and P, are massive applied in food production (Šimanský et al., 2022; Lim et al., 2021; Eurostat, 2013; Smith et al., 1999) to improve crop yield (Rina et al., 2014). Nitrogen use continues rise globally with 110 Mt/year (Bijay-Singh and Craswell, 2021) and nitrogen excess pollutes a large number of surface and groundwaters around the world, becoming it in a global problem.

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In OECD (Organization for Economic Cooperation and Development) countries, nitrates level in groundwater exceeds between 10 and 15 % on average the limit of 50 NO_3mg/L set by the WHO (World Health Organization) (Mateo-Sagasta and Marjani, 2018), which represents a risk to environment (Fernández-Martínez et al., 2020; Kurtzman et al., 2013) and to health in many different ways (Riedel et al., 2022), with evidence of a relationship between some diseases and this type of pollution (Picetti et al., 2022; García-Garizábal et al., 2012).

Nitrogenous fertilizers use, both mineral and organic mainly from manures, and also pesticides, in agriculture appears as a common denominator in studies about polluted aquifers in all parts of the world (Abascal et al., 2022; Böhlke, 2002), accepting agriculture as one of the main sources of diffuse pollution on water bodies (Richa et al., 2022; Lim et al., 2021; Johnes, 1996; Pérez-Martín et al., 2016; Dorado-Guerra et al., 2021).

Phosphorus use has also increased strongly, more than 6 times, since the 1950s, through the massive utilization of phosphate from rocks (Ashley et al., 2011). Globally, 38 % phosphorus that reaches to surface waters comes from agricultural uses, with runoff being the main source of contribution to lakes and estuaries (Mateo-Sagasta and Marjani, 2018). Some authors show the great inefficiency in phosphorus application, indicating that a maximum of 25 % of the phosphorus applied in a year is used by plants for their growth, while the rest becomes part of the soil or water (Morgan, 1997 in Eurostat, 2013). Massive use of phosphorus, 20 Mt/year, along with nitrogen excess, has become a global problem of water eutrophication (Ashley et al., 2011), with a N:P global ratio of nitrogen and phosphorus use of 5.5.

In current situation of growing food demand and food security need (Tomlinson, 2013) and, therefore, greater use of fertilizers, it is necessary to improve optimization of fertilizers application to real needs of crops (Bacenetti et al., 2020; Kurtzman et al., 2013) and therefore, reduce pollution levels (Bishayee et al., 2022). Transmission from technical and scientific advances to water end users can help to achieve an improvement in water resources use (Re et al., 2017), increasing or maintaining yield production and decreasing nitrate and phosphorus levels in waters. More in detail, reducing fertilizer use to the optimal dose it does not represents a crop yield loss and it reduces cost production and pollution to the environment.

Although there are technologies that allow to reduce nitrates in already contaminated aquifers (Bishayee et al., 2022; Richa et al., 2022) or reducing nitrate from effluents (Mehrabinia et al., 2022), reduction on fertilizers application and consequently nitrogen surplus is one of the most effective measures to reduce nitrates levels in groundwater (Puertes et al., 2021; Pérez-Martín et al., 2016).

At a global view, objective number 6 of Sustainable Development Goals (Ensure access to water and sanitation for all) aims to guarantee water and sanitation universally. Specifically, point 6.3 states that by 2030 water quality should be improved by reducing pollution (UN, 2018). At European level, legislation has implemented different strategies, the most important relative to agricultural sustainability is the Farm to Fork strategy (EC, 2020), located at the center of the European Green Deal (EC, 2019), which aims to make food systems fair, healthy and environmentally friendly. Specifically, this strategy sets as one of its objectives for the year 2030 the reduction of nitrogen losses by 50 % and establishes a 20 % reduction in the use of fertilizers by 2030 as a means of obtain it.

Compatibility between agricultural production, food security and pollution reduction in the environment requires the use of tools, such as nutrient balances (NBs), and models that evaluate effectiveness of measures in the environment for different doses of fertilizer application. Simulation models of crop growth and nitrogen leaching allow estimating nitrogen used by plants and nitrogen leaching to the aquifer. These models reproduce nitrate transport in soil and the aquifer, in such a way that determine the temporal evolution of nitrogen or nitrate. There are mathematical models of soil nitrogen transport, such as: ENVIRO-GRO (Pang and Letey, 1998), LEACHM (Hutson and Wagenet, 1995) or a review included in Van der Laan et al. (2014): RZWQM (Ma et al., 1998; Hanson et al., 1998), GLEAMS (Webb et al., 2001), APSIM (Keating et al., 2003), CropSyst (Stöckle et al., 2003), CERES, CROPGRO and CANEGRO within the DSSAT framework (Daroub et al., 2003, Van der Laan et al., 2011), and SWB-Sci (Van der Laan, 2010). HYDRUS (Šimůnek et al., 1988), although not a crop model, has also been used extensively to simulate N leaching (Phogat et al., 2013). And there are mathematical models of nitrate transport in the aquifer such as MT3D-USGS model (Bedekar et al., 2016) and mathematical models of nitrogen transport in soil and in the aquifer for large basins such as PATRICAL model (Pérez-Martín et al., 2016).

The use of these models makes possible to evaluate the effect of different fertilizer management measures, such as: a 50 % decrease in fertilizers used by farmers would mean a 70 % reduction in nitrates without significantly affecting production (Kurtzman et al., 2013); 10 % reduction in water irrigation and fertilizers at the same time would reduce leachate by 5.5 % more than reducing fertilizers alone (Phogat et al., 2014); or for *Citrus Reticulata* crop, that a 30 % reduction in irrigation during the optimal period can lead to a 37 % decrease in percolated water and in 52 % leached nitrogen compared to the initial situation (Phogat et al., 2014).

Models also suggest that irrigation system used in crops has an important influence on the production of nitrogen leachate (Vaughan and Letey, 2015) and phosphate runoff, which ends up contaminating groundwater and surface water (Schepers et al., 1995); the application of localized irrigation decreases total volume of water and can reduce leachates, in addition to improving the efficiency of fertilizers applied through fertigation (García-Garizábal et al., 2012; Alva et al., 2006; Cassel Sharmasarkar et al., 2001) increasing water productivity by 26.4 % and nitrogen use efficiency by 34.3 % (Li et al., 2021); So, the change from surface irrigation to drip irrigation can mean, on average, reductions of 2 % in volume of water recharge and 15 % in nitrogen leachate (Pool et al., 2022), or reduce nitrogen leaching from 33 % in flood irrigation to 18 % in drip irrigation (Pool et al., 2022).

Nutrient balances, nitrogen and phosphorus, are widely used, due to ease parameterization, availability to have long-term data, and relatively reduced execution time (Lynch et al., 2019; Van der Laan et al., 2014), in the regional, national or supranational territorial scope, by different organizations -OECD, EU (European Union)- that elaborate these balance calculations to improve the agricultural and environmental management of their respective territories (OECD, 2021; EEA, 2019). Such as at the European level, balances are used to calculate agro-environmental indicators required for implementation of Rural Development Program, Water Framework Directive (WFD) (EC, 2000) and Nitrates Directive (e.g. location of vulnerable areas) (Eurostat, 2013).

These balances are one of the main indicators considered in research related to surface and groundwater pollution (Andrade et al., 2022). While an excess of these nutrients can have negative impacts on the environment, their deficiency can mean loss of soil fertility and worsening of agricultural production yields. (Eurostat, 2013). In this way, balances also have been used to estimate causes of soil impoverishment and suggest changes in management that increase fertility, considering the combined use of organic and inorganic compounds (e. g. Ethiopia, Bedada et al., 2016). Nutrient balances are also frequently used in combination with mathematical models (Jakrawatana et al., 2017; Ricci et al., 2022).

Soil represents the largest phosphorus (P) stock in terrestrial ecosystems (He et al., 2021), it is presented in soil in two forms, as organic P and inorganic P, and in three main pools: solution pool, active pool and fixed pool. Around 80 % of this phosphorus is immobile and not available for uptake by plants, corresponding with all organic P and a part of inorganic P (Prasad and Chakraborty, 2019). Solution pool is the smallest pool, it is the pool from which plants can uptake phosphorus, plant-available phosphorus (Olsen-P), and is formed by inorganic P dissolved in water/soil solution, as HPO_4 and H_2PO_4, inorganic phosphates, and a small amount of organic phosphorus. Active or labile pool, which releases phosphorus to solution pool that can be up taken by plants, is formed by adsorbed phosphorus, inorganic P attached to clay or Fe and Al oxides in soil, secondary minerals CA, Fe, Al phosphates and organic phosphorus that mineralize easy. Fixed pool (or non-labile), which release phosphorus from this pool extremely slow to the active pool, is the largest pool and it is formed by mineral P present in soil, by primary minerals like apatite, and by organic phosphorus that do not mineralize easy. The three pools are in equilibrium with each other if solution pool is depleted by plants then phosphorus is replenished by active pool, reverse also is done. Maintaining soil near the critical level should optimize yield and the global use of P while minimizing the risk of transfer large amounts of P to the aquatic environment (Johnston and Poulton, 2019).

When phosphorus fertilizer is applied to croplands, which are often deficient in native P for optimal plant growth, only a small portion is taken up by the crop and about 2 % is lost in dissolved forms in runoff waters. The rest of the added P is adsorbed to soil minerals and accumulates in the soil as a legacy, this accumulated P is known as legacy-P (Gatiboni et al., 2020; Bian et al., 2022). Legacy-P may contribute to future plant growth, but also it is lost to the environment (Schlesinger, 2021).

Mathematical models are used to determine the advantages to use drip irrigation in agricultural areas, reducing nitrate leaching to the aquifer (Pool et al., 2022) or establishing nutrient application strategies in drip irrigation, such as applying fertigation at the end of drip irrigation to reduce more nitrate leaching (Azad et al., 2019). However, the novelty of this work is how to assess the effect of these measures in the environment, specifically how contribute to recovery a heavy nitrate polluted aquifer and a long-time entropized lake.

Three tools: Nutrient Balance (NB), ENVIRO-GRO model and PATRICAL model, are applied in this work in a combined way to assess the effect of modernize an irrigation system in nutrients losses (both nitrogen and phosphorus), from traditional flood irrigation to drip irrigation, for citrus fruits crops in the Jucar basin in Spain. NB of nitrogen and phosphorus is used to evaluate the application of nutrients and losses that occur with traditional flood irrigation and drip irrigation. ENVIRO-GRO model is applied to simulate the water/nitrogen cycle in the soil and to determine surface runoff, infiltration and nitrogen leaching into the aquifer. PATRICAL model is used to evaluate the effect on nitrate levels in the "Plana Valencia Sur" aquifer and the time required to recover the aquifer to good status. And finally, is evaluated the effect of the reduction in phosphorus losses that reach to the long-time eutrophicated RAMSAR Albufera lake (Martín et al., 2020).

2. Study area and meteorological data

Jucar River Basin District (JRBD) is located in Mediterranean side of the Iberian Peninsula (Ferrer et al., 2012) and covers an area of 42,735 km^2 (Fig. 1). Groundwater resources represents 80 % of global resources in the JRBD with around one hundred groundwater bodies. Near the coast and associated to the Ramsar Albufera lake it is located the Plana Valencia Sur (PVS) aquifer (566 km^2), which has a disponible water resources of 156 hm^3/year and only 21 hm^3/year has agriculture and farm uses, so its quantitative status is quite good (CHJ, 2022). Over this aquifer there are a very intensive irrigated crops, such as citric, fruit trees, vegetables and rice, so this aquifer is one of the most polluted aquifers by nitrates of the 21 with poor chemical status by nitrates in the JRBD (CHJ, 2022), according with the Jucar River Basin Management Plan (JRBMP), due to its nitrate levels are above the limit of 50 mgNO$_3$/L.

JRBD management plan for 2022–2027 (CHJ, 2022) considers that there are around 374,000 ha of agricultural use in the river basin, 20,500 ha of them corresponds to the Acequia Real del Jucar (ARJ), the main irrigated area that is located over PVS aquifer. ARJ is a canal managed by the same name irrigation community in Jucar river left bank. ARJ is one of the largest and oldest, more than 200 years, irrigation communities in the country with 20,500 ha of total irrigable surface, where 13,700 ha of them are citrus, persimmon and fruit plantations, and 4500 ha are rice fields. ARJ is immersed in a modernizing process of its irrigation infrastructure that began in 2001, changing from flood to drip irrigation. Currently, it has 20 of its 45 sectors modernized, 17 of which are fully operational. Water surplus from ARJ, with also nitrogen and phosphorus, returns to the drainage network and reach the 50-year eutrophicated Albufera lake (Martín et al., 2020), and also pollute the PVS aquifer by nitrates.

Monthly climate data is obtained from Spanish Meteorological Agency (AEMET) meteorological stations, such as (Table 1): precipitation (mm/month), minimum temperature (°C), maximum temperature (°C), air humidity (%), wind speed (km/day), isolation (number of solar hours). From meteorological data and crop coefficient, for citrus (Kc), is obtained by using CROPWAT (Smith, 1992) and applying FAO Penman-Monteith formula (Allen et al., 1998): potential evapotranspiration for reference crops (ETo, mm/day), potential evapotranspiration for citrus (ETc, mm/month) and effective rainfall (EffRain, mm/month).

Mediterranean climate is characterized by a mild temperature variation between winter (daily mean 12 °C) and summer (daily mean 26 °C), also, with a small daily thermal range, difference between maximum and minimum daily temperature, with around 9 °C, also this climate has low relative air humidity and high solar insolation. Under these conditions evapotranspiration of the reference crop is 1280 mm/year. Annual rainfall is around 475 mm/year, so climate aridity index (ETo/P = 2.9) clearly indicates that it corresponds with a semiarid region (Liu et al., 2019). Citrus evapotranspiration ETc (817 mm/year) is obtained multiplying ETo to citrus crop coefficient, which value (kc = 0.65) is obtained from other studies about irrigation demands in the region (Pérez-Martín et al., 2022).

3. Methods and models

A different set of tools and models have been used to determinate the effect of fertigation in nitrate levels in the Plana Valencia Sur aquifer and

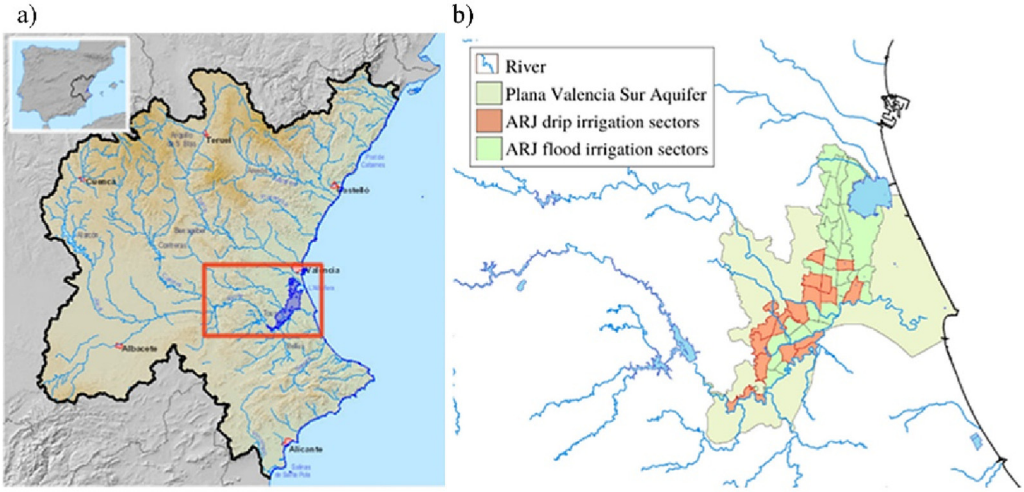

Fig. 1. a) Jucar River Basin District (JRBD) and b) Plana the Valencia Sur location (PVS).

Table 1

Climate data from AEMET from meteorological stations: precipitation, temperature, air humidity, wind speed and isolation. Evapotranspiration for reference crop ETo, crop coefficient for citrus Kc, potential evapotranspiration Etc for citrus and effective rainfall.

Month	Precipitation	Tmin	Tmax	Air humidity	Wind speed	Isolation	ETo	Kc (coef,)	ETc	EffRain
	mm/month	°C	°C	%	km/day	hours	mm/day	Dimensionless	mm/month	mm/month
Oct	77	15.2	24.3	67	242	210	3.1	0.69	66.9	67.4
Nov	47	10.8	19.8	66	251	180	2.2	0.69	47.4	43.5
Dec	48	8.1	17.0	65	251	150	1.8	0.69	40.2	44.2
Jan	37	7.1	16.4	64	251	180	1.9	0.70	41.8	35.0
Feb	36	7.8	17.1	64	251	180	2.3	0.70	44.9	33.8
Mar	33	9.6	19.3	63	251	240	3.1	0.68	65.4	31.3
Apr	38	11.5	20.8	62	242	240	3.8	0.65	73.4	35.6
May	39	14.6	23.4	65	233	240	4.3	0.61	82.2	36.5
Jun	22	18.6	27.1	66	190	270	4.9	0.60	87.7	21.3
Jul	8	21.5	29.7	67	190	300	5.4	0.60	99.5	7.9
Aug	20	21.9	30.2	68	190	270	5.0	0.60	91.3	19.4
Sep	70	19.1	27.9	67	233	240	4.2	0.61	76.0	62.1
Year	**475**	**13.8**	**22.8**	**65**	**231**	**2700**	**1280**	**0.65**	**816.7**	**438.0**

phosphorus loads to the eutrophicated Albufera lake (Fig. 2). A review of water and fertilizers, nitrogen and phosphorus, used for flood and drip irrigation in citric was carried out, by one-to-one interview with owners (final farmers) and managers of the ARJ irrigation system. Also, a review of surface and groundwater chemical network is done.

An accurate nutrient balance (NB) for nitrogen is done from data collected from users for a range of scenarios, three in flood irrigation and two in drip irrigation conditions. Nutrient balance includes all inputs: application by farmers, nitrogen atmospheric deposition, and nitrogen in irrigation water, and the main outputs: plant uptake and volatilization. Also, ENVIRO-GRO model was used to simulate for the five scenarios nitrogen movement through soil and to obtain nitrogen leaching to the aquifer.

Both, nutrient balance (NB) and ENVIRO-GRO model determinate nitrogen excess (surplus) produced in citric crops, for flood irrigation and for drip irrigation. Phosphorus excess is obtained, which is washed by surface runoff during flood irrigation or during rainfall storms and flows until the Albufera lake contributing to its eutrophication. Nitrogen excess is washed by surface runoff and is also infiltrated to the aquifer. PATRICAL model, previously calibrated, is used to analyse nitrogen leaching impact in the aquifer nitrate levels, and to determine time needed to aquifer recovery, by reducing nitrate levels under legal limit of 50 mgNO_3/L.

3.1. Nitrogen leaching model (ENVIRO-GRO)

ENVIRO-GRO model is a free one-dimensional, transient-state model of soil water flow and chemical transport designed specifically for agricultural applications (Pang and Letey, 1998). The model provides relative crop yield predictions and considers the effects of water and nutrient stress on plant growth, as well as nitrogen uptake by crops and nitrogen leaching (Fig. 3). This model is used in studies about nitrate leaching and soil nitrate content (Allaire-Leung et al., 2001). Model simulates subsurface variably-saturated water flow (Richard's equation), solute transport, root water uptake (under stressed or non-stressed conditions), nitrogen uptake, and relative yield for agricultural applications. Nitrogen module uses a convection-dispersion equation and includes nitrate transport, organic nitrogen fertilization incorporated through tillage, inorganic nitrogen fertilization, organic nitrogen mineralization through a standard decomposition process, and compensation of nitrogen uptake. (Letey and Vaughan, 2013).

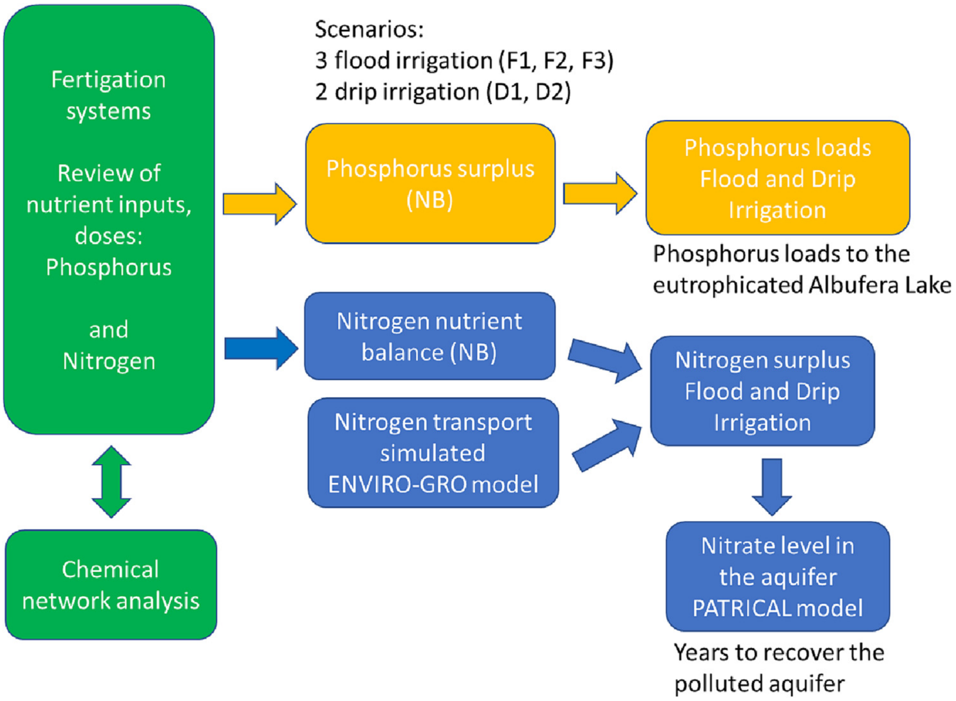

Fig. 2. Developed methodology.

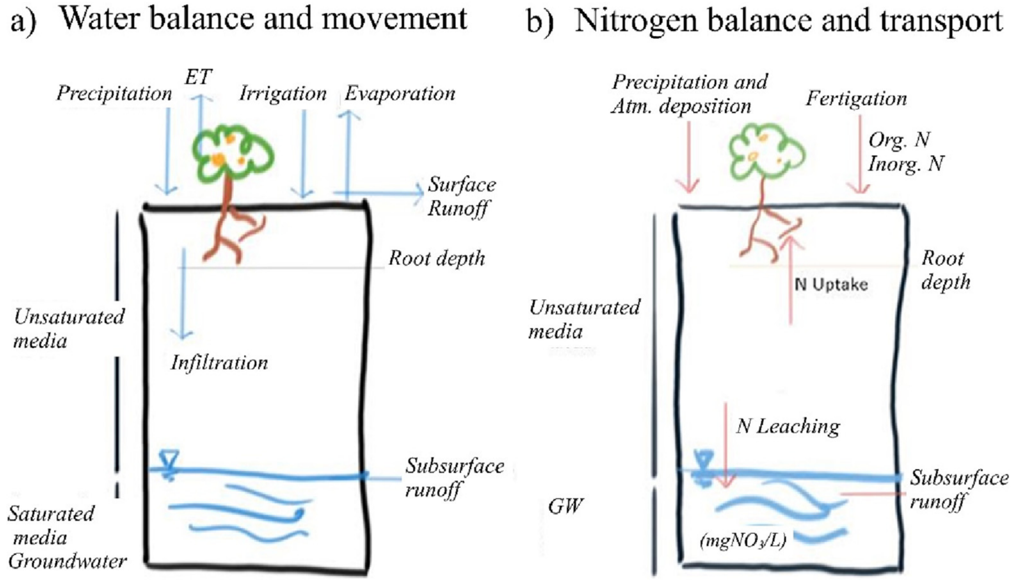

Fig. 3. ENVIRO-GRO model, a) water movement and water balance module and b) nitrogen balance and transport module.

Input data in ENVIRO-GRO includes: vertical layer geometry; time step and simulation period; soil hydraulic properties and chemical transport; crop properties (planting date, intermediate and final harvesting, daily evapotranspiration and plant nitrogen uptake curve); daily effective precipitation; irrigation schedule and chemical properties; nitrogen applications including dose and date for organic and mineral sources, and, finally, initial conditions for water and nitrogen. Model provides daily water and nitrogen NO_3-N flux and ratio between computed and potential N uptake.

Five-year simulation for each scenario was simulated, with daily time step, considering only balance results of last year, to remove initial conditions effect. Soil properties selected for this area correspond with clay loam soil with free drainage and plant properties correspond with adult stage citrus (Table 2).

Three types of water inputs with different chemical properties are prepared, first one for precipitation, second one for flood irrigation and third one for drip irrigation. Monthly precipitation in the Mediterranean area tends to concentrate in a few days (Homar et al., 2018), so it produces more runoff and more infiltration in precipitation events and it also produces more nitrogen losses. Different rainfall length events were considered to obtain sensitivity of results to this factor. Combining these results with rainfall events length from observed data it was considered that concentrate monthly precipitation in five days can better reproduce this behavior (Domingo, 2015).

Irrigation events are delayed fifteen days with respect precipitation events to simulate the real conditions of management developed by the owners. Drip irrigation system is simulated every day according to annual plan of the ARJ community, and it is stopped during precipitation events and not restart until three days after the precipitation event. Water irrigation in the ARJ area comes directly from the Jucar river (Tous reservoir), both for flood irrigation and drip irrigation, water analyses indicates that nitrate concentration is 6 $mgNO_3/L$ for nitrogen and between 0.02 and 0.05 mgP/L for phosphorus.

Table 2
Soil and plant parameters used in ENVIRO-GRO.

System	Parameter	Value
Soil	Volumetric saturated water content (θs) (cm^{-1})	0.41
Soil	Volumetric residual water content (θr)	0.095
Soil	Saturated hydraulic conductivity (Ks) ($cm{\cdot}d^{-1}$)	6.24
Soil	α-shape parameter (cm^{-1})	0.019
Soil	n-shape parameter (cm^{-1})	1.31
Soil	Bulk density ($g{\cdot}cm^{-3}$)	1.40
Soil	Molecular diffusivity ($cm^2{\cdot}d^{-1}$)	0.026
Soil	Mechanical dispersity (cm)	8.1
Plant	Maximum rooting depth (cm)	1.30
Plant	Threshold stress for matric head (cm)	−879
Plant	Permanent wilting point (cm)	−7121
Plant	Maas-Hoffman threshold salinity (dS/m)	1
Plant	Maas-Hoffman slope (percent reduction %/(dS/m)	13
Plant	Maximum rooting depth (cm)	130

3.2. PATRICAL model

PATRICAL model (Pérez-Martín et al., 2016), is a nitrogen transport model for large basins widely used in Spain, in the context of Water Framework Directive implementation, to determine: aquifer nitrate levels, necessary measures to recovery the aquifer and time needed. PATRICAL model is a large-scale (medium/large RBs), conceptual, monthly and spatially distributed (grid 1 × 1 km^2) water balance (Pérez-Martín et al., 2014) and water quality model (Pérez-Martín et al., 2016), for multi-decadal periods 50–100 years. Description of hydrological model - components, water storages and fluxes and hydrological parameters - its calibration and application to the Júcar RBD - is addressed in Pérez-Martín et al. (2014). Nitrate module has three storages in each cell (i.e. 1 × 1 km), (Fig. 4b): 1) Soil Storage, where nitrogen is in soil moisture. 2) Unsaturated Zone, between root zone and GW level. 3) Aquifer, which corresponds with saturated zone, where a complete mixing of substances in water is considered. Nitrate model was previously calibrated for the Jucar River Basin District (Pérez-Martín et al., 2016). In this model non-point source (NPS) pollution - nitrogen surplus (Fig. 4a) - comes mainly from fertilizers, manures and deposition, it is located in top soil and is carried by water, as nitrate, by surface runoff and infiltration into the aquifer.

Nitrogen surplus is retained in soil (Fig. 4b), where volatilization and water transport are produced. Nitrate is carried by surface runoff to rivers and by infiltration to the unsaturated zone. Nitrate is retained in the unsaturated zone, where retained amount depends on unsaturated thickness, which is the difference between surface and monthly simulated GW level. Nitrate in the unsaturated zone is washed out by deeper infiltration into the aquifer. Aquifer is considered as an aggregate element and GW discharges represent nitrate aquifer outputs. 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.

PATRICAL model is used to analyse the future evolution of nitrate levels in the Plana Valencia Sur aquifer considering two agricultural practices: first one associated to current system, flood irrigation, and second one

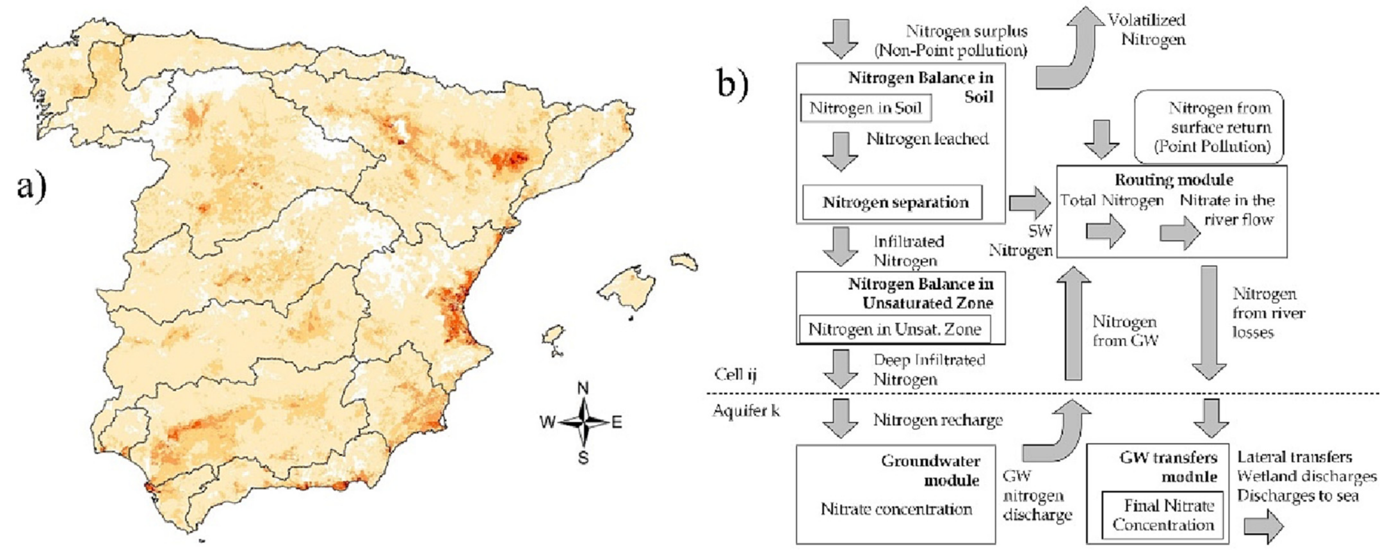

Fig. 4. a) Distributed nitrogen surplus (kgN/ha/year) and b) structure and variables of the nitrate module of PATRICAL model (Pérez-Martín et al., 2016).

associated with a 50 % reduction in nitrogen losses according with the European Green Deal.

4. Results and discussion

4.1. Water and nutrient application with flood and drip irrigation

Water and nutrient management are analyzed including a wide range of cases, 5 scenarios, that cover a totally realistic and extreme practices in the region. Three for traditional system - flood irrigation - (F1, F2 and F3), depending on number of fertilizations done, and two for modernized system - drip irrigation - (D1 and D2).

Flood irrigation system consists in apply water by flooding fields from one side to other side that requires each time around 900 m^3/ha/application. Around 8 times in a year are applied in this area, one flooding per month in March, April, May, and June, and two flooding per month in the most intensive and hot season of July and August, each 15–21 days. This system uses large amount of water 7200 m^3/ha/year and produces great water losses both by surface runoff and infiltration to lower layers to the aquifer. Fertilizers are applied directly to field in two ways: mineral fertilizers and manures, which includes organic fertilizers and organic matter. Also, large amounts of sulfates (SO_3) are applied in flood irrigation to reduce fungal growth due to high soil moisture.

Drip irrigation system consists in apply water every day during one to three hours, during all the year, but mainly from April to November. This system reduces the amount of water applied, 4400 m^3/ha/year, and water losses, because no produce runoff and minimize infiltration to the aquifer. In this system soil moisture variations are lower because it is possible to better control soil moisture near roots. Fertigation consists in apply liquid fertilizers, both mineral and organic, dissolved in water and distribute it by the irrigation network. It allows to apply nitrification inhibitors that reduce the nitrification decreasing nitrate leaching risk. Significant amount of organic matter is added in drip irrigation, around 22.4 kg/ha/year, probably with the aim of increase phosphorus mineralization from the active pool to solution pool and therefore releases plant-available forms of phosphorus into soils, due to the addition of organic matter can efficiently improve P availability (Yang et al., 2018).

Flood irrigation scenarios (Table 3) have a range of nutrient total inputs from a low level of nutrients 180 kgN/ha/year and 26 kgP/ha/year (F1-COPAL) to an extreme application of nutrients considering extra direct organic application by farmers (F2-Owners + OM) 300 kgN/ha/year and 52 kgP/ha/year. Drip irrigation scenarios have lower application of fertilizers with 123 kgN/ha/year and 2.4 kgP/ha/year (D1-ARJ) and even in an unrealistic extreme scenario (D2-high-end), equivalent to F3-high-end scenario, created to explore what happens if end-users add manures directly to the field.

Monthly water and nutrient application schedule correspond for first scenario (F1-COPAL) with management developed by the Agricultural Cooperative of Algemesí in Spain (COPAL), which approximately manages 10 % of municipal term irrigation surface. This scenario considers only two applications of fertilizer (Table 4), with around 180 kgN/ha/year and 26 kgP/ha/year, one in March with 120 kgN/ha/year and 13kgP/ha/year other in June with 60 kgN/ha/year and 13 kgP/ha/year. Second one scenario (F2-Owner), with around 250 kgN/ha/year and 37 kgP/ha/year, corresponds to direct management by owners (final farmers) derived from one-to-one interview and considers three applications of fertilizer, same as previous scenario plus another application in August to improve fertilization with 60 kgN/ha. It is considered that most of the fields are fertilized within the range of these two scenarios. Finally, third scenario, extreme scenario, (F3-High-end) is based on scenario F2 with an extra application of manure in April (60 kgN/ha/year and 15kgP/ha/year), so considers four applications of fertilizers per year with 310 kgN/ha/year and 52 kgP/ha/year. This last scenario incorporates strong uncertainties produced when farmers apply manures directly in the field.

Other inputs are added in all scenarios, such as: atmospheric deposition (7 kgN/ha/year) and nutrients included in water irrigation (9.8 kgN/ha/

Table 3
Annual water, nitrogen and phosphorus applied for flood and drip irrigation.

Scenario	Manager	Fertilizer schedule	Water (m^3/ha/year)	Apply N (kgN/ha/year)	Apply P (kgP/ha/year)
F1-COPAL	COPAL	2 applies	7200.0	180.5	26.3
F2-Owner	Owners	3 applies	7200.0	246.7	36.8
F3-high-end	Owners + OM	F2 + 1 apply with OM	7200.0	306.9	51.8
D1-ARJ	ARJ	Fertigation Mar. - Nov.	4437.2	123.1	2.4
D2-high-end	ARJ + OM	D1 + 1 apply with OM	4437.2	180.5	17.4

Table 4
Monthly water, nitrogen and total phosphorus applied in flood irrigation for scenarios F1, F2 and F3.

N	Flood irr. applied water (m^3/ha)	Irr. water (kgN/ha)	Athm. dep. (kgN/ha)	F1-COPAL apply N (kgN/ha)	F2-owners apply N (kgN/ha)	F3-High-end apply N (kgN/ha)	F1-COPAL total N (kgN/ha)	F2-Owners total N (kgN/ha)	F3-High-end total N (kgN/ha)
Oct	0.0	0.00	0.58	0.00	0.00	0.00	0.58	0.58	0.58
Nov	0.0	0.00	0.58	0.00	0.00	0.00	0.58	0.58	0.58
Dec	0.0	0.00	0.58	0.00	0.00	0.00	0.58	0.58	0.58
Jan	0.0	0.00	0.58	0.00	0.00	0.00	0.58	0.58	0.58
Feb	0.0	0.00	0.58	0.00	0.00	0.00	0.58	0.58	0.58
Mar	900.0	1.22	0.58	0.00	120.34	120.34	1.80	122.14	122.14
Apr	900.0	1.22	0.58	120.34	0.00	60.20	122.14	1.80	62.00
May	900.0	1.22	0.58	0.00	0.00	0.00	1.80	1.80	1.80
Jun	900.0	1.22	0.58	0.00	63.18	63.18	1.80	64.98	64.98
Jul	1800.0	2.44	0.58	60.17	0.00	0.00	63.19	3.02	3.02
Aug	1800.0	2.44	0.58	0.00	63.18	63.18	3.02	66.20	66.20
Sep	0.0	0.00	0.58	0.00	0.00	0.00	0.58	0.58	0.58
TOTAL	**7200.0**	**9.76**	**6.96**	**180.51**	**246.70**	**306.90**	**197.23**	**263.42**	**323.62**

P	Flood irr. applied water (m^3/ha)	Irr. Water 0.02 mgP/L (kgP/ha)	Irr. Water 0.05 mgP/L (kgP/ha)	F1-COPAL apply P (kgP/ha)	F2-Owners apply P (kgP/ha)	F3-high-end apply P (kgP/ha)	F1-COPAL total P (kgP/ha)	F2-owners total P (kgP/ha)	F3-High-end total P (kgP/ha)
Oct	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nov	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dec	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Jan	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Feb	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mar	900.0	0.02	0.05	13.14	26.27	26.27	13.17	26.31	26.31
Apr	900.0	0.02	0.05	0.00	0.00	15.00	0.03	0.03	15.03
May	900.0	0.02	0.05	0.00	0.00	0.00	0.03	0.03	0.03
Jun	900.0	0.02	0.05	13.14	0.00	0.00	13.17	0.03	0.03
Jul	1800.0	0.04	0.09	0.00	0.00	0.00	0.06	0.06	0.06
Aug	1800.0	0.04	0.09	0.00	10.51	10.51	0.06	10.57	10.57
Sep	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	**7200.0**	**0.14**	**0.36**	**26.27**	**36.78**	**51.78**	**26.53**	**37.04**	**52.04**

year and 0.1 to 0.4 kgP/ha/year). Atmospheric deposition is obtained from the Spanish nitrogen balance for this region Mapama, 2018a. Nitrogen content in water is obtained considering mean nitrate concentration in water of 6 $mgNO_3$/L that is representative of water used for irrigation from Tous reservoir. Total input for flood irrigation in citrus ranges from 197 kgN/ha/year and 27kgP/ha/year, in lower case, until 263–324 kgN/ha/year and 37–52 kgP/ha/year depending on the amount of applied manures in the field.

Applied nutrients have a N:P ratio around 6 and 7, a value slightly higher than the average value of 5 for citrus in the region (Mapama, 2018a, b), or global value 5.5 obtained from global use of fertilizers 110 MtnN/year (Bijay-Singh and Craswell, 2021) and 20 MtP/year (Ashley et al., 2011). So, phosphorus application in this area in slightly lower than in other areas, probably due to the great amount of phosphorus storage in soil during the more than 100 years of agricultural activities in this area as documented elsewhere in the world (Zhang et al., 2022).

Monthly drip irrigation and fertigation data have been obtained from real schedule of the Acequia Real del Jucar (ARJ) and from interviews with owners. Drip irrigation applies 4400 m^3/ha/year mainly between April and November, and fertigation (adding nutrients to water) is developed between March and September (Table 5), because fertilization it is not allowed during fall and winter to reduce nitrate leaching. D1-ARJ scenario corresponds with usual fertigation developed by the ARJ, 123 kgN/ha/year and 2.4 kgP/ha/year. Also, it is added an extreme an unrealistic scenario (D2-High-end scenario) to explore what would happen if manures were directly applied in the field by end-users with an extra application of manure of 60 kgN/ha and 15 kgP/ha/year equal as flooding case. In both scenarios other inputs are added, such as: atmospheric deposition (7 kgN/ha/year) and nutrients included in water irrigation (9.8 kgN/ha/year and 0.1 to 0.2 kgP/ha/year). Total input for D1-ARJ drip irrigation scenario is 136 kgN/ha/year and 2.52 kgP/ha/year.

Phosphorus applied in the ARJ is only 2.5 kgN/ha/year, ratio N:P = 52, this value is well below to 20 kg/ha/year that would correspond if N:P ratio of 6 was maintained. These data, together with organic matter addition show that the most technical irrigation seeks to take advantage of existing phosphorus reserve in soil, phosphorus legacy, and reduce external contributions.

Summarizing results by managers, management developed by final users (F2-Owners) applies large amounts of nitrogen (247 kgN/ha/year) and phosphorus (37 kgP/ha/year). Management carried out by agricultural technicians (F1-COPAL) applies a more adjusted amount of nitrogen (180 kgN/ha/year) and phosphorus (26 kgP/ha/year); finally, ARJ fertigation applies a more reduced amount of nitrogen (123 kgN/ha/year) and phosphorus (2.4 kgP/ha/year). There is around 50 % reduction between nitrogen applied by Owners (F2-Owners) with flood irrigation and ARJ (D1-ARJ) with drip irrigation.

4.2. Chemical control network

To analyse the effect of flood irrigation and drip irrigation on the aquifer and river chemical status, a selection of chemical measurement points is done from the JRBD Official Surface Water (SW) and Groundwater (GW) control networks (Fig. 5) that have data of nitrogen and phosphorus from 2007 but in an unsystematic way.

GW stations of the Plana Valencia Sur aquifer located in areas non-modernized, with traditional flood irrigation system, have nitrate levels stabilized around 140 and 160 $mgNO_3$/L. By the other hand, there is only one station (08-144-CA003, source of Green river) in areas affected by modernization with data before and after modernization. This station is located inside the area affected by modernization done in Sector VI of ARJ in 2010 and has only two data available before modernization and it has enough data after modernization. Data shows (Fig. 6) that nitrate levels drop down from 100 $mgNO_3$/L to around 40 $mgNO_3$/L in one year because the point is located inside modernized area and the effect is observed very quickly. To obtain conclusions for the entire aquifer it is required more data to evaluate the effects of modernization in other areas.

SW network measures groundwater drainages in this point, Massalaves spring and Green river, and confirms lower nitrate levels in this area

Table 5
Monthly water, nitrogen and total phosphorus applied in drip irrigation for scenarios D1 and D2.

N	Drip irr. applied water (m^3/ha)	Irr. water (kgN/ha)	Athm. dep. (kgN/ha)	D1-ARJ apply N (kgN/ha)	D2-hign-end apply N (kg/ha)	D1-ARJ total N (kgN/ha)	D2-High-end total N (kgN/ha)
Oct	348.0	0.47	0.58	0.00	0.00	1.05	1.05
Nov	285.0	0.39	0.58	0.00	0.00	0.97	0.97
Dec	45.0	0.06	0.58	0.00	0.00	0.64	0.64
Jan	75.0	0.10	0.58	0.00	0.00	0.68	0.68
Feb	90.0	0.12	0.58	0.00	0.00	0.70	0.70
Mar	90.0	0.12	0.58	9.29	21.30	9.99	22.00
Apr	102.0	0.14	0.58	14.56	14.56	15.28	15.28
May	375.8	0.51	0.58	17.15	17.15	18.24	18.24
Jun	528.8	0.72	0.58	27.92	27.92	29.22	29.22
Jul	764.2	1.04	0.58	20.04	20.04	21.66	21.66
Aug	876.8	1.19	0.58	16.37	16.37	18.14	18.14
Sep	856.6	1.16	0.58	17.81	17.81	19.55	19.55
TOTAL	**4437.2**	**6.02**	**6.96**	**123.14**	**135.15**	**136.12**	**148.13**

P	Drip irr. applied water (m^3/ha)	Irr. water 0.02 mgP/L (KgP/ha)	Irr. water 0.05 mgP/L (KgP/ha)	D1-ARJ apply P (KgP/ha)	D2-high-end apply P (KgP/ha)	D1-ARJ total P (kgP/ha)	D2-High-end total P (kgP/ha)
Oct	348.0	0.01	0.02	0.00	0.00	0.01	0.01
Nov	285.0	0.01	0.01	0.00	0.00	0.01	0.01
Dec	45.0	0.00	0.00	0.00	0.00	0.00	0.00
Jan	75.0	0.00	0.00	0.00	0.00	0.00	0.00
Feb	90.0	0.00	0.00	0.00	0.00	0.00	0.00
Mar	90.0	0.00	0.00	1.18	1.18	1.19	1.19
Apr	102.0	0.00	0.01	0.00	15.00	0.00	15.00
May	375.8	0.01	0.02	0.00	0.00	0.01	0.01
Jun	528.8	0.01	0.03	0.00	0.00	0.02	0.02
Jul	764.2	0.02	0.04	1.18	1.18	1.21	1.21
Aug	876.8	0.02	0.04	0.00	0.00	0.03	0.03
Sep	856.6	0.02	0.04	0.00	0.00	0.03	0.03
TOTAL	**4437.2**	**0.09**	**0.22**	**2.36**	**17.36**	**2.52**	**17.59**

compared with rest of the aquifer. Current phosphorus levels in surface water that collects surface irrigation returns is around 0.1–0.3 mgP/L, unfortunately, these points do not have enough data to establish any conclusion about what happens with phosphorus before and after the modernization. Despite the extensive surface and groundwater chemical network, location and temporary availability of data is not enough to clearly well determine at present the effects of modernized sectors in the aquifer and in water returns from crops.

4.3. Modelling nitrogen balance by ENVIRO-GRO

4.3.1. Water balance

Same five scenarios have been simulated by ENVIRO-GRO model, three for flood irrigation (F1, F2 and F3) and two for drip irrigation (D1 and D2). Model provides both daily water and nitrogen balance in soil for five years simulated. To eliminate effects of initial conditions, only last year is taken as representative year to analyse results. Drip irrigation schedule for

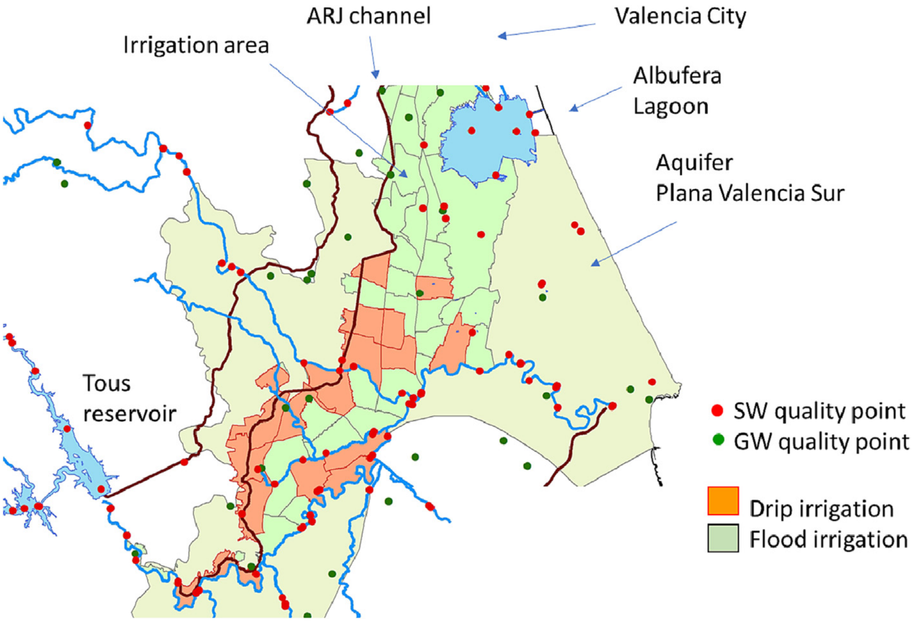

Fig. 5. SW and GW quality networks and modernized (drip) and traditional (flood) irrigation systems.

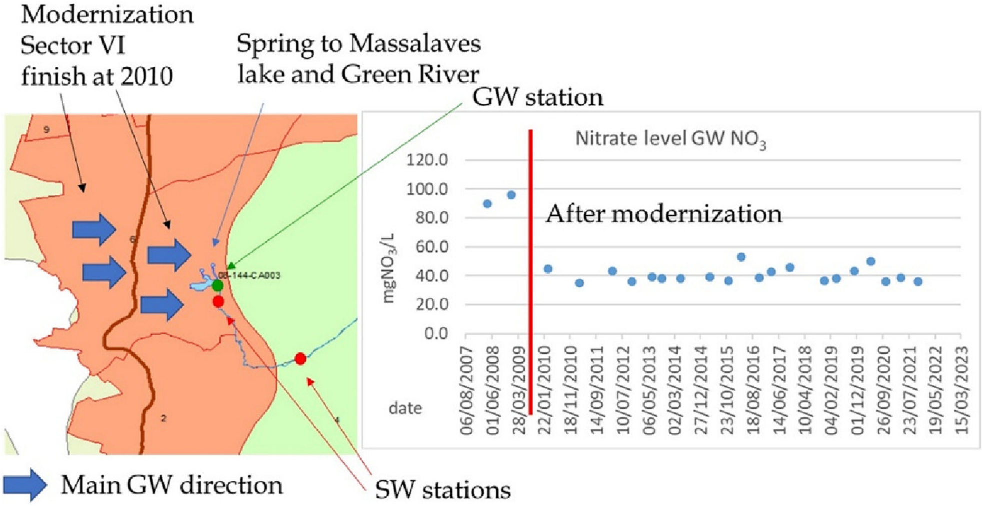

Fig. 6. Evolution of nitrate levels in GW at 08-144-CA003 control point before and after modernization of the irrigation system, spring of the Green river.

water and nitrogen application has been optimized starting from ARJ schedule to maintain soil moisture and available nitrogen during growing season and to reduce infiltration and nitrogen leaching.

Soil moisture have similar values in both systems around 150 and 300 mm, however drip irrigation can maintain soil moisture more constant around 150 and 250 mm, with a daily application of water, so it significantly reduces infiltration (Fig. 7). In flood irrigation, infiltration clearly occurs during two periods fall and summer. In fall, infiltration is associated with rainfall and, in summer, it is associated with irrigation.

In flood irrigation, total water contributions are 1160 mm/year (Table 6), 440 mm/year from rainfall and 720 mm/year from water irrigation, which last one is equivalent to 7200 m^3/ha/year. The large amount of water applied produces a surface runoff during flood irrigation of 184 mm/year and an infiltration to the aquifer of 162 mm/year. Rest of water is evapotranspiration done by crops 805 mm/year. Infiltration represents 14 % related to total applied water and a loss of 22.5 % of applied irrigation water. Total losses, infiltration and surface runoff, represent 48 % of applied irrigation water, which it is a usual value of efficiency in flood irrigation systems (application efficiency of 50 %). Crops are not stressed because difference between ETc and ETR is lower than 1 %.

In drip irrigation system, water applied is lower than flood system, with 444 mm/ha/year (4400 m^3/ha/year), so total water input to the soil is 888 mm/ha/year. Surface runoff disappears, and total infiltration is reduced to 76–89 mm/ha/year. Under optimized irrigation schedule crops are not stressed with less than 1 %. Water losses represent 17–20 % of water applied, so water application efficiency of the irrigation system is around 0.8.

Plant growth needs, and therefore current evapotranspiration ETR, are related to available water and nitrogen. This explains slight variations in water balance between scenarios within same irrigation method since it would imply different levels of nitrogen stress.

Difference between water applied between two systems is 2800 m^3/ha/year that represents a water save of 37 % respect flood irrigation. Infiltration is reduced from 22 % to 17–20 % in drip irrigation, like other results reported previously in this area from 19 % to 16 % (Pool et al., 2022). Water losses (including surface runoff and infiltration) are reduced from the 48 % in flood irrigation to 20 % in drip irrigation, so irrigation excess loaded with nutrients, nitrogen (mainly in infiltration) and phosphorus (only in surface runoff) is reduced to less than half. As is mentioned, surface runoff is zero for drip irrigation, so phosphorus pollution is greatly reduced.

4.3.2. Nitrogen balance

Plant uptake needs of 120 kgN/ha/year is considered for citrus, and nitrogen volatilization is estimated in 7 % of total nitrogen inputs. This value represents double amount of nitrogen than atmospheric deposition, which is an adequate proportion for an intensive cropping area.

In flood irrigation, nitrogen fertilization is manual or mechanical, applied in two (F1-COPAL), three (F2-Owners) or four (F3-High-end) specific moments. The highest amount of nitrogen application occurs in March when 120 kgN/ha is applied in one day (Fig. 8 top). In drip irrigation (D1-ARJ), fertigation (fertilization through drip infrastructure) is applied almost continuously between March and October, finding a maximum level of nitrogen applied with 0.93 kgN/ha/day.

In flood irrigation, the available nitrogen increases immediately after nitrogen application and subsequently starts to decrease (Fig. 8). Available nitrogen ranges between 50 and 360 kgN/ha depending on flood scenario considered. When flood irrigation with water excess of rainfall is produced the available nitrogen is washed by infiltration and reaches to the aquifer. Other side, the continuous application of fertilizers in drip irrigation avoids peaks in the available nitrogen, which ranges from 50 to 100 kgN/ha in D1-ARJ scenario and between 180 and 220 kgN/ha if the extreme D2-High-end scenario was produced.

Nitrogen losses into the aquifer (Fig. 8) in flood irrigation are clearly related to infiltration during summer and fall, due to infiltration washes nitrate from soil. In drip irrigation is much lower in both scenarios.

In the case of flood irrigation, total nitrogen applied is between 196 kgN/ha/year (F1-COPAL) and it is 322 kgN/ha/year for the extreme scenario (F3-high-end) (Table 7). Nitrogen uptake reaches plant needs (120 kgN/ha/year) in all scenarios with nitrogen stress under 1 %. Nitrogen leaching increases from 60 kgN/ha/year in scenario F1 to 120 kgN/ha/year in scenario F2. Nitrogen losses are between 30 % and 46 % refer to total nitrogen applied. Surface nitrogen losses, related to surface water runoff, are 3.6 kgN/ha/year for this irrigation method. For the extreme scenario F3 nitrogen leaching can rise to 55 %. Results show that nitrogen application over technical based recommendations done by COPAL, around 180 kgN/ha/year, implies an overfertilization that do not increase production but increases strongly nitrate leaching to the aquifer.

In drip irrigation system, D1-ARJ scenario, nitrogen application is optimized, with total nitrogen applied of 136 kgN/ha/year, crops are slightly stressed, around 4 %, and nitrogen leaching is strongly reduced to 17.5 kgN/ha/year, which represents less than 13 % of total nitrogen applied. Finally, surface losses disappear.

For the extreme D2-high-end scenario, with 183 kgN/ha/year if additional manures are applied, the large application of manures in soil (60kgN/ha) produces that available nitrogen in soil are similar to the flood scenarios, nitrogen leached rise to 58 kgN/ha/year, which represents 30 % of total nitrogen applied. So, clearly doses applied by ARJ are the optimal and additional doses only increase pollution to the aquifer.

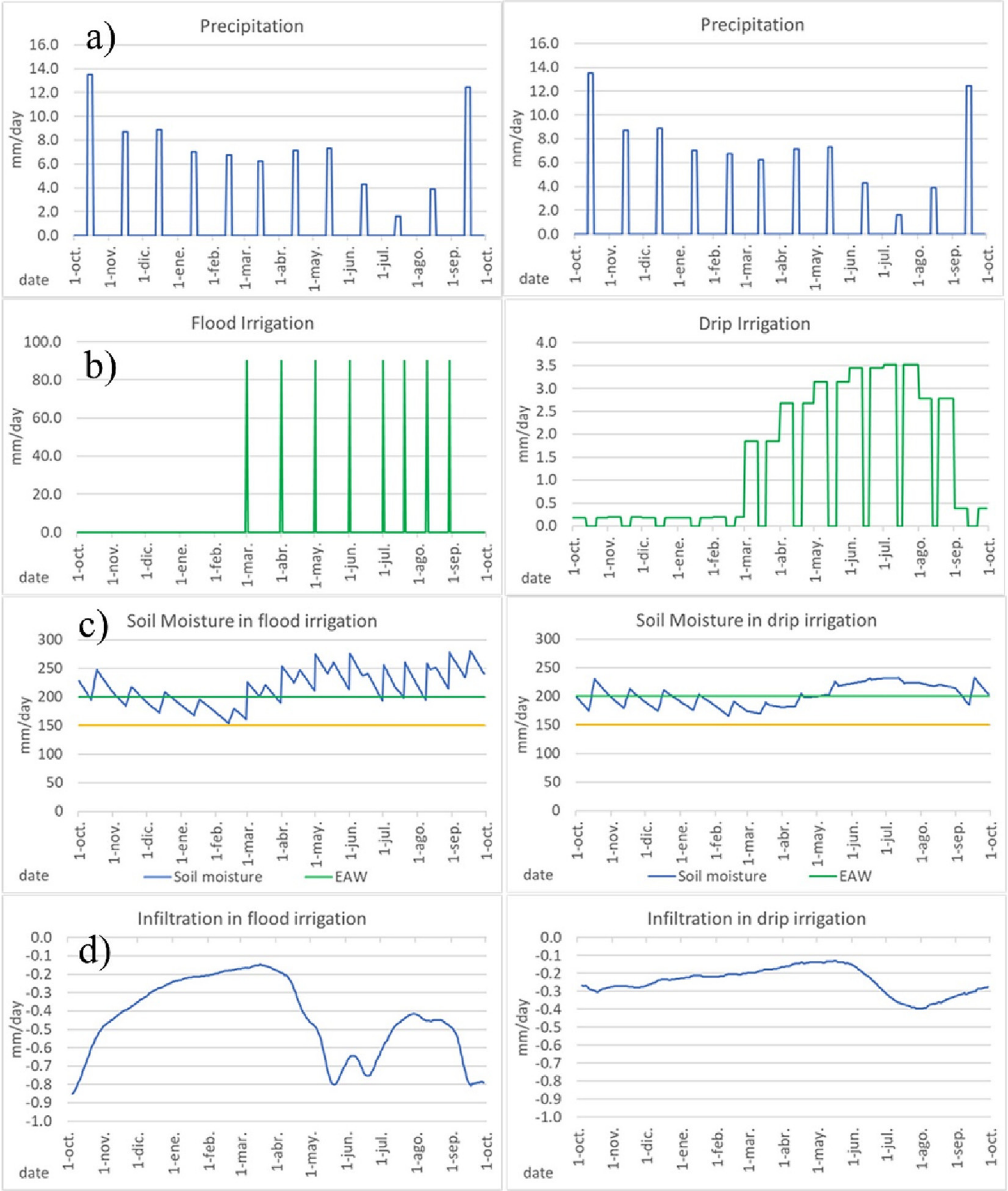

Fig. 7. Daily water balance for flood (left) and drip (right) irrigation. From up to down: a) precipitation (mm/day), b) irrigation (mm/day), c) soil moisture (mm) and d) infiltration (mm/day).

4.4. Nitrogen leaching curves and phosphorus legacy

Nutrient Balance (NB) and ENVIRO-GRO model results are combined to better determinate nitrogen losses for flood irrigation and drip irrigation systems (Fig. 9). Both methods obtain similar results, in case of total nitrogen inputs of 200 kgN/ha/year nitrogen leaching is greater than 60 kgN/ha/year, increasing linearly from this value. For nitrogen inputs of 250 kgN/ha/year nitrogen leaching is around 100 kgN/ha/year or more.

Fertigation reduces nitrogen leaching from 60 to 120 kgN/ha/year produced by flood irrigation to 18 kgN/ha/year in fertigation. Nitrogen losses are reduced in a range of 71–86 % refer to flood results, being higher than 50 % established by the European Union. In relative terms, nitrogen losses changes from 30 to 60 % for flood irrigation to 20 % for drip irrigation cases, quite similar to values reports in other studies with reductions from 33 % to 18 % (Pool et al., 2022). Besides, application of fertigation at the end of irrigation can reduce more nitrate leaching (Azad et al., 2019).

Phosphorus applied in flood irrigation ranges from 26 kgP/ha/year to 52 kgP/ha/year, taking in account short amount of phosphorus is removed from surface runoff during irrigation events, major part of phosphorus excess is retained in soil increasing the amount of phosphorus stored, as phosphorus legacy. Obtained results for this area are in the same order than regional nutrient balance based on regional statistics, where phosphorus surplus is estimated in 66 KgP/ha/year for citric in this region. Phosphorus applied in drip irrigation is 2.6 kgP/ha/year (D1-ARJ scenario) that represents a reduction between 90 % and 95 % refer to flood irrigation, so it demonstrates that currently there is a large content of phosphorus in soil, corresponding to phosphorus legacy. This modernized system tries to mobilize this amount of phosphorus, by adding organic matter to soil, rather than adding more phosphorus by fertilizers (Rakotoson et al., 2015; Wang et al., 2021). Phosphorus fertigation by drip irrigation system may offer an effective way to alleviate the soil and water pollution caused by the excessive input of phosphorus fertilizer (Xiao et al., 2020).

Table 6
Water annual balance for flood irrigation and drip irrigation.

Water balance	F1-COPAL	F2-Owner	F3-high-end	D1-ARJ	D2-high-end
Precipitation (mm/year)	438.0	438.0	438.0	438.0	438.0
Irrigation (mm/year)	720.0	720.0	720.0	450.3	450.3
Total applied water (mm/year)	**1158.0**	**1158.0**	**1158.0**	**888.3**	**888.3**
Soil Water (mm/year)	973.5	973.6	973.4	890.4	890.4
Surface Runoff (mm/year)	184.5	184.4	184.6	0.0	0.0
Total water input (mm/year)	**1158.0**	**1158.0**	**1158.0**	**890.4**	**890.4**
ETR (mm/year)	805.1	805.1	808.2	798.9	805.1
Infiltration (mm/year)	159.3	158.3	157.6	89.3	76.1
Total output (mm/year)	**964.4**	**963.4**	**965.8**	**888.2**	**881.2**
Balance error (mm)	9.1	10.2	7.6	2.2	9.2
Balance error (%)	0.9 %	1.1 %	0.8 %	0.2 %	1.0 %
ETc (mm/year)	812.6	812.6	812.6	812.6	812.6
ETR (mm/year)	805.1	805.1	808.2	798.9	805.1
Water Stress: Etc-ETR (mm)	7.5	7.5	4.4	13.7	7.5
Relative Water Stress	0.9 %	0.9 %	0.5 %	1.7 %	0.9 %
Infiltr./Total Water (%)	13.8 %	13.7 %	13.6 %	10.1 %	8.6 %
Infiltr./Irrigation (%)	22.1 %	22.0 %	21.9 %	19.8 %	16.9 %
Irrigation losses (%)	**47.8 %**	**47.6 %**	**47.5 %**	**19.8 %**	**16.9 %**

Nutrient ratio N:P (nitrogen: phosphorus) allows to know nutrient needs by plants, a review N:P ratio for different plants is included in Güsewell (2004), where values ranges from 9.1 for subarctic evergreen woody (Eckstein and Karlsson, 1997) to 18.6 for European wetlands evergreen woody (shrubs) (Güsewell and Koerselman, 2002). In the Mediterranean area (Greece), evergreen woody has 16.6 N:P ratio, deciduous woody has 15.1 ratio and herbaceous (mainly forbs) has 14.0 ratio (Margaris et al., 1984). For healthy citrus N:P ratio is around 18 for *Citrus reticulata*, around 10 for *Citrus limon* and around 12 for *Citrus maxima* (Cao et al., 2015). In general terms, N:P ratio for plants are around 14–16 but typical fertilizer ratio N:P is around 5.5, so phosphorus proportion is three times higher in fertilizers. Results show that N:P ratio pass from 7.5 for flood irrigation to 52 in drip irrigation, taking advantage of the large amount of phosphorus included in the sediment.

In both systems direct application of manures by owners (final user) produce strong uncertainties about the amount of extra nutrients that are applied to the soil and how many of them can reach the aquifer.

4.5. Effect in nitrate levels in the aquifer and Albufera lagoon

Application of drip irrigation in whole ARJ citrus area, 13,700 ha, has two significant effects in relation to nutrient losses: first one, nitrogen leaching reduction that pollutes the Plana Valencia Sur aquifer; and second one, phosphorus excess reduction that reduces the amount of phosphorus in soil, the phosphorus legacy, and also reduces phosphorus washed by surface runoff during flood irrigation that reach the Albufera lake, which during last 50-years presents significant problems of eutrophication (Martín et al., 2020).

In relation to nitrate levels in the aquifer, PATRICAL model (Pérez-Martín et al., 2016) is used to simulate the effect of nitrate leaching by crops in nitrate levels in the whole aquifer. Simulations (Fig. 10) show that current applications of nitrogen, for the most part associated which flood irrigation, keep mean nitrate level in the aquifer between 70 and 80 $mgNO_3/L$, above legal limit of 50 $mgNO_3/L$. In the worst and more intensive agricultural area nitrate levels in the aquifer are stabilized around 140 NO_3/L, such as is observed in chemical groundwater network.

Plana Valencia Sur aquifer has two main crops citrus (and other fruit trees) and rice. Only citrus (and other fruit trees) can be modernized from flood to drip irrigation, reducing nitrate leaching from 60–120 kgN/ha/year to 18 kgN/ha/year, which represents around 71–86 % reduction in nitrogen excess. Expanding this reduction to the whole aquifer, can be considered with a conservative hypothesis that nitrogen excess reduction, which can around 80 %, in drip irrigation area, can reduce globally the nitrogen excess by 50 % in the entire aquifer. It should be note that, aquifer most polluted areas are located where citrus flood irrigation is produced at present, so the effect will be greater in these areas.

PATRICAL model obtains that mean nitrate level in the aquifer can fall below 50 $mgNO_3/L$ in 5–6 years after the complete implementations of measures (Fig. 10), nitrate levels would stabilize around 40 $mgNO_3/L$ value slightly higher than the limit to declare the aquifer at risk.

Historical phosphorus load to the Valencia lake were estimated at 78.6 tnP/year (Martín et al., 2020), in recent years these contributions have been reduced to 60–65 tn/year thanks to implementation of additional waste water treatment measures (CHJ, 2022). Main phosphorus contributions to the lake come from irrigation surpluses surrounding the lake (51 %) from irrigation systems of Jucar and Turia rivers. Total irrigation returns from ARJ (irrigation system in Jucar river) to the Albufera lake are estimated on 121 hm^3/year, with a phosphorus concentration of 0.12 mgP/L, produces a total load of 13.9 tnP/year (CHJ, 2022) that represents 23 % of total loads to the lake. Part of theses returns come from irrigation runoff surpluses from the 13,700 ha of citrus, which can be estimated on 25.2 hm^3/year with a concentration of 0.35 mgP/L and produce a phosphorus contribution of 8.8 tnP/year, which represents 15 % of total phosphorus input to the Albufera lake. Drip irrigation transformation produces that these contributions disappearance due to surface runoff and surface phosphorus drag disappear in this irrigation system, contributing to reduce total phosphorus loads to the lake and improving its environmental recovery.

5. Conclusions

Based on the results, which are representative of citrus crops in the Mediterranean area, transformation from traditional flood irrigation to more technical system of water and nutrient manage with drip irrigation reduces de amount of water and nutrients applied. Water application is reduced in 37 % eliminating water excess by surface runoff and slightly reducing infiltration, from 22 % to 17 %, as also is reported by other authors. Nutrient application is also significantly reduced, both nitrogen with 30 %, values much higher than the 20 % established by the European Strategy, Farm to Fork, of European Green Deal, and phosphorus with 90 %.

Nitrogen application can change from non-full technical decision and with great dispersion between 180 kgN/ha/year and 247 kgN/ha/year to more technically based and supervised amount of 136 kgN/ha/year. More significantly, phosphorus can change from 26 to 37 kgP/ha/year in flood irrigation to 2.6 kgP/ha/year in drip irrigation.

Based on information collected and uncertainties analysis in determining total application of nitrogen and phosphorus by the different users, a centralized decision system supported by technicians to determine the

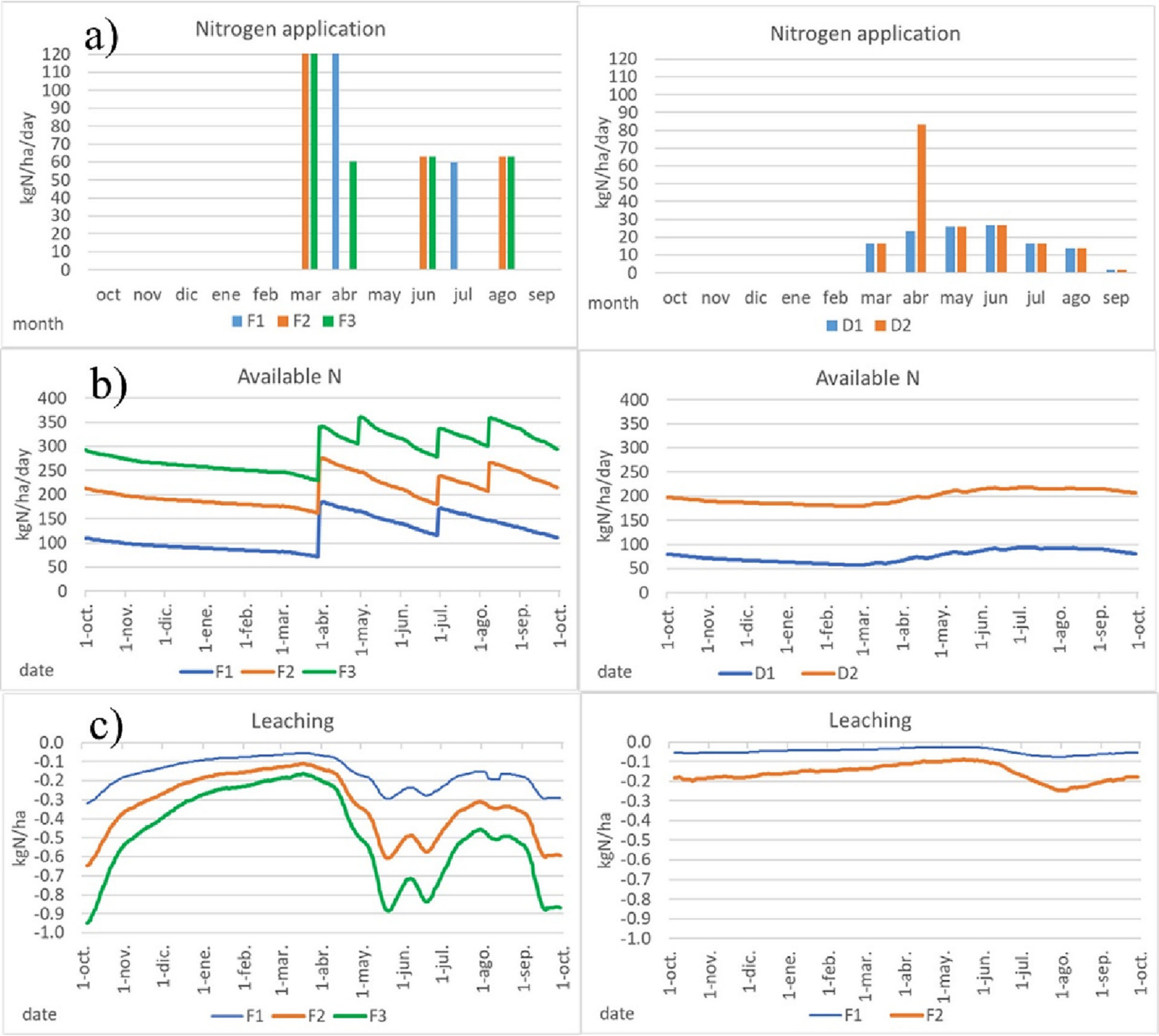

Fig. 8. Daily nitrogen balance for flood (left) and drip (right) irrigation. From up to down a) daily nitrogen applied, b) daily available nitrogen in soil and c) leached nitrogen in kgN/ha/year.

dose applied is more adjusted to real needs of crops and therefore produces a significant reduction in nitrogen and phosphorus losses and, then, reduces final pollution in the environment. Also, in fertigation, water and fertilizers application is carried out distributed over time with a dose more adjusted to real needs of crops at each moment, in such a way that the punctual application of water and fertilizers is avoided, which produces greater losses of water, nitrogen and phosphorus.

Nitrogen losses are obtained by nutrient balance and by detailed simulation of soil made with ENVIRO-GRO model. Annual results with ENVIRO-GRO model are quite similar to results obtained with nutrient balance. Model clearly shows how nitrogen is washed away with irrigation excess and with infiltration during rainfall events. In traditional flood irrigation, nitrogen leaching occurs during two periods: in summer during irrigation campaign and in the autumn related to the wet period. In case of drip

Table 7
Nitrogen Balance for flood and drip irrigation scenarios.

Nitrogen balance	F1-COPAL	F2-Owner	F3-high-end	D1- ARJ	D2-high-end
Fertigation (kgN/ha/year)	180.5	246.7	306.0	123.0	183.0
Irr. Water + Atm. Dep. (kgN/ha/year)	16.2	16.2	16.2	13.0	13.0
Total N inputs (kgN/ha)	**196.7**	**262.9**	**322.2**	**136.0**	**196.0**
Plant needs (kgN/ha/year)	119.9	119.9	119.9	119.9	119.9
Simulated N uptake (kgN/ha/year)	118.9	119.1	119.5	115.0	119.6
Volatilization (kgN/ha/year)	13.8	18.4	22.6	0.0	13.7
Lecahing N (kgN/ha/year)	59.4	120.6	176.9	17.5	57.9
N surface losses (kgN/ha/year)	3.6	3.6	2.8	0.0	0.0
Total N outputs (kgN/ha/year)	**195.7**	**261.7**	**321.8**	**132.5**	**191.3**
Balance error (kg/ha/year)	1.0	1.2	0.4	3.5	4.7
Balance error (%)	0.5 %	0.5 %	0.1 %	2.6 %	2.4 %
Nitrogen Stress (%)	0.8 %	0.6 %	0.4 %	4.1 %	0.2 %
Leaching (%)	30.2 %	45.9 %	54.9 %	12.8 %	29.6 %

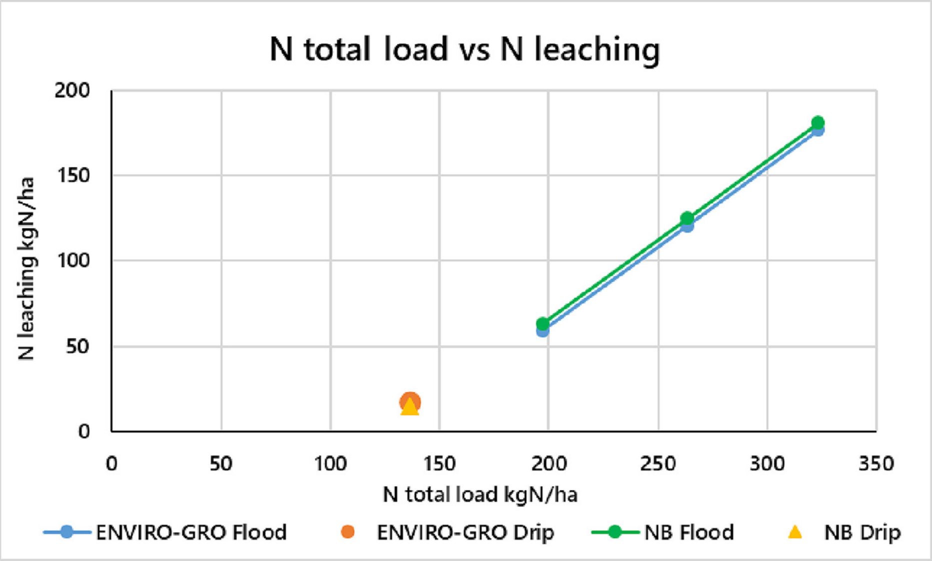

Fig. 9. Nitrogen leaching curves from nutrient balance and simulation for flood and drip irrigation.

irrigation, nitrogen leaching is much lower. Obtained results show that nitrogen losses in the case of fertigation are reduced between 71 % and 86 %, a value much higher than the 50 % reduction objective established by the European Union.

In both cases, flood irrigation and drip irrigation, adding more fertilizers than recommended doses by irrigation communities, COPAL 180 kgN/year for flood irrigation and ARJ 123 kgN/year for drip irrigation, do not increase significantly plant growth but strongly increase nitrogen losses that finally go to the environment.

Plana Valencia Sur aquifer, where the irrigation analyzed areas are located, is currently in poor chemical status due to nitrates pollution. Nitrate levels in the studied area are between 70 and 150 mgNO$_3$/L, values well above the maximum admissible value of 50 mgNO$_3$/L or the value to declare it at risk of poor condition of 37.5 mgNO$_3$/L. Based on obtained results with PATRICAL model, it is possible to recover the aquifer in around 5–6 years after implement of modernized irrigation systems are completed. Nitrogen losses reduction applied in this irrigation area, around 71 %–86 %, is compatible with the general goal of 50 % reduction in nitrogen excess (nitrogen losses) for the entire aquifer, which is established in the Jucar River Basin Management Plan to recover the aquifer groundwater good status. These values fit perfectly with the European Farm to Fork Strategy of the European Green Deal, which establishes a 50 % reduction in nitrogen losses by 2030 through a 20 % reduction in nitrogen application.

Main components of phosphorus cycle are limited to surface runoff, without infiltration or volatilization, so phosphorus surplus is only dragged by surface waters during extreme rain events or during flood irrigation excess. Phosphorus excess is retained in soil, increasing phosphorus storage, forming the phosphorus legacy that can reach the Albufera lake by erosion during heavy rainfall events. Current modernized fertigation significantly reduces phosphorus application, around 90 %–95 %, surface runoff disappears during irrigations events, so diffuse phosphorus contributions from this area to the Albufera lake are eliminated. These contributions can represent a 20 % of total current contributions to the lake, so it contributes to reduce the eutrophicated state of the lake. In addition, phosphorus content in soil, called the phosphorus legacy, will be reduced so phosphorus loads during extreme rainfall events will also be reduced.

Fig. 10. Nitrate levels in Plana Valencia Sur without measures and with measures (50 % reduction of nitrogen excess).

CRediT authorship contribution statement

Miguel Ángel Pérez-Martín: Conceptualization; Formal analysis; Funding acquisition; Investigation; Methodology; Project administration; Resources; Software; Supervision; Validation; Visualization; Roles/Writing – original draft; Writing – review & editing.

Sara Benedito-Castillo: Data curation; Formal analysis; Investigation; Methodology; Software; Supervision; Validation; Visualization; Roles/Writing – original draft; Writing – review & editing.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Sara Benedito Castillo reports financial support was provided by Acequia Real del Júcar. Miguel Angel Perez-Martin reports financial support was provided by Acequia Real del Júcar. Miguel Angel Perez-Martin reports financial support was provided by Government of Spain Ecological Transition Ministry.

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