Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria (INIA)
Available online at www.inia.es/sjar

Spanish Journal of Agricultural Research 2011 9(3), 924-937
ISSN: 1695-971-X
eISSN: 2171-9292

# Evaluation of nitrate leaching in a vulnerable zone: effect of irrigation water and organic manure application

M. Ruiz-Ramos[1], J. L. Gabriel[2], N. Vazquez[3] and M. Quemada[2]*

[1] *Instituto de Ciencias Ambientales. Universidad de Castilla-La Mancha. Avda. Carlos III, s/n. 45071 Toledo, Spain*

[2] *Departamento de Producción Vegetal: Fitotecnia. Universidad Politécnica de Madrid (UPM). Avda. Complutense, s/n. 28040 Madrid. Spain*

[3] *Centro de Investigación y Desarrollo Agrario (CIDA). NA-134, km 88. 26071 La Rioja. Spain*

## Abstract

Sustainable agricultural practices are needed to minimize nitrate leaching. The crop-soil simulation model STICS coupled with a geographic information system was used to estimate the amount of $NO_3^-$ leaching and to assess the ability of alternative management practices to reduce $NO_3^-$ leaching in a nitrate vulnerable zone (NVZ) in La Rioja, Spain. Model performance was examined by comparing the simulations and measurements of irrigated grapevine crops (variety Tempranillo) over various soil types. The measurements were obtained from five pilot plots over a period of three years and included the mineral nitrogen, the water content of the soil profiles and the nitrogen content of the crops. The simulated and measured values were in satisfactory agreement with each other. Then, eight management scenarios were simulated, combining two $NO_3^-$ concentrations of irrigation water and four levels of organic manure applications. The simulations identified good agricultural practices (GAP) for mitigating $NO_3^-$ pollution. High soil mineral nitrogen (SMN) and water pollution were driven by both the $NO_3^-$ concentration of irrigation water and the level of organic manure application. The use of aquifer water for irrigation would lead to diminish aquifer pollution at the expense of maintaining high SMN, non desirable for grape quality production. River water would offer an opportunity for the recovery of soils and the improvement of underground water quality if the application of organic manure was limited according to soil type. Differences in $NO_3^-$ leaching of the NVZ soils depended more on their ability to store N than on their annual drainage.

Additional key words: GIS; good agricultural practices; nitrogen; STICS; vineyards.

## Resumen

### Lavado de nitratos en una zona vulnerable: efectos del agua de riego y de la aplicación de abono orgánico

Las prácticas agrícolas sostenibles son necesarias para minimizar el lavado de nitratos ($NO_3^-$). Se utilizó el modelo de simulación de cultivos STICS para estimar el lavado de $NO_3^-$ y evaluar prácticas de manejo para reducirlo en una zona vulnerable (NZV) en La Rioja, España. Se compararon las simulaciones con las medidas en cultivos de vid en regadío (variedad Tempranillo) en distintos tipos de suelo. Las medidas de nitrógeno mineral, contenido en agua en el suelo y contenido en nitrógeno de los cultivos se obtuvieron en cinco parcelas piloto durante tres años. Las simulaciones mostraron una coincidencia satisfactoria con las medidas. Después, se simularon ocho escenarios de manejo, combinando dos concentraciones de $NO_3^-$ en el agua de riego y cuatro niveles de abonado orgánico. Las simulaciones permitieron identificar buenas prácticas agrícolas (GAP) para la mitigación de la contaminación por $NO_3^-$. Tanto la concentración de $NO_3^-$ en el agua de riego como el nivel de abonado orgánico determinaron la contaminación del agua y el alto nitrógeno mineral del suelo. Regar con agua del acuífero reduciría la contaminación del acuífero a expensas de mantener alto el nitrógeno mineral del suelo, no deseable para la producción de uva de calidad. Regar con agua del río permitiría recuperar los suelos mejorando la calidad del agua subterránea, si el abonado orgánico se limitase en función del tipo de suelo. Las diferencias en el lavado de $NO_3^-$ de los suelos de la NVZ dependieron más de su capacidad para almacenar N que de su drenaje anual.

**Palabras clave adicionales**: buenas prácticas agrícolas; nitrógeno; SIG; STICS; viñedos.

* Corresponding author: miguel.quemada@upm.es
Received: 30-06-10. Accepted: 25-05-11.

## Introduction

Aquifer contamination due to $NO_3^-$ leaching has received special attention in European Union legislation because diffuse pollution has significantly increased in many areas of intensive agriculture (EC, 2000). The sustainability of cropping systems in these areas depends on the development of agricultural techniques that maintain farm profitability while minimizing the deleterious effects of pollution on groundwater. Diffuse pollution at the catchment scale is difficult to estimate because of uncertainties due to transfer time, spatial variability, and the diversity of farming practices (Beaudoin *et al.*, 2008). Crop simulation models coupled with geographic information systems (GIS) may help to overcome these limitations and allow for the identification of agricultural practices that mitigate $NO_3^-$ pollution of groundwater (Trabada-Crende and Vinten, 1998; De Paz and Ramos, 2004; Ledoux *et al.*, 2007).

Several simulation models have been used to estimate the leaching of $NO_3^-$ below the root zone. Some process-based models are able to simulate the effects of a large variety of agricultural practices (Stöckle and Nelson, 1994; Tsuji *et al.*, 1994; Brisson *et al.*, 2003). These models focus not only on the dynamics of N and water in the soil, but also on crop N uptake. However, crops are often considered simply as sinks for N, with crop activity estimated using N extraction coefficients or average yields. Models that simulate crop development and growth can improve the estimation of N uptake by crops and, therefore, the assessment of potentially leachable N. Crop models require detailed input data to be validated, but offer more reliable evaluations of the outcomes of alternative farming practices based on more realistic seasonal patterns of N uptake; consequently, these models provide better estimates of $NO_3^-$ leaching (Brisson *et al.*, 2003).

The Ebro Valley, located in northeast Spain, is an area with abundant intensive irrigated agriculture and a resulting serious groundwater contamination problem (MMA, 2004). In 2000, part of the valley feeding the quaternary aquifer of Aldeanueva (La Rioja, North Spain) was included in a national list compiled in response to an EU directive as a well-documented example of groundwater degradation due to land use (EC, 1991). Excessive fertilizing and frequent overwatering of crops were common practices in the past but are currently limited; they have resulted in serious $NO_3^-$ contamination of groundwater, with concentrations exceeding 30 mg N $L^{-1}$ (Zeta Amaltea, 2005).

The objective of the work presented here was to evaluate the close link between crop management and groundwater protection in the nitrate vulnerable zone (NVZ) by quantifying the $NO_3^-$ leaching that is occurring below the rooting zone in irrigated vineyards on various soil types, and to assess the ability of alternative management practices to reduce $NO_3^-$ leaching. In this case the target NVZ, representative of other irrigated areas of Mediterranean Europe, serves to compare scenarios combining different levels of $NO_3^-$ concentration of irrigation water and organic manure application.

## Material and methods

### The study area

The site under investigation measured approximately 850 ha and was located over a perched aquifer that is associated with a glacis and is connected to the large alluvial aquifer of the Ebro River in La Rioja (North Spain, Fig. 1). A hydrological study conducted by the *Confederación Hidrográfica del Ebro* (Zeta Amaltea, 2005) established that the perched aquifer transfers a total of 0.627 $hm^3$ of water per year to the alluvial aquifer. With an average $NO_3^-$ concentration of 31.7 mg N-$NO_3^-$ $L^{-1}$, the $NO_3^-$ transfer amounts to 20.32 Mg N annually.

Irrigated vineyards have been progressively replacing horticultural crops in the area since the 1990s. By 2000, vineyards covered more than 95% of the region's cropland (MAPA, 2001). During this time, good agricultural practices (GAP) were encouraged, particularly concerning irrigation and water recirculation (using water previously extracted from the aquifer), but aquifer sources

Abbreviations used: E (coefficient of efficiency); E treatment ($NO_3^-$ in the irrigation water equivalent to 6 mg N $L^{-1}$); GAP (good agricultural practices); GIS (geographic information systems); MAE (mean absolute error); NCU (nitrogen crop uptake); NVZ (nitrate vulnerable zone); P treatment ($NO_3^-$ in the irrigation water equivalent to 32.7 mg N $L^{-1}$); R0 treatment (no application of organic manure); R1 treatment (application of organic manure equivalent to 60 kg N $ha^{-1}$ every two years); RMSE (root mean square error); RN treatment (application of organic manure equivalent to 170 kg N $ha^{-1}$ per year); RZ treatment (application of organic manure equivalent to 331 kg N $ha^{-1}$ per year); SMN (soil mineral nitrogen); STICS (crop-soil model Simulateur mulTIdisciplinaire pour les Cultures Standards); SWC (soil water content).

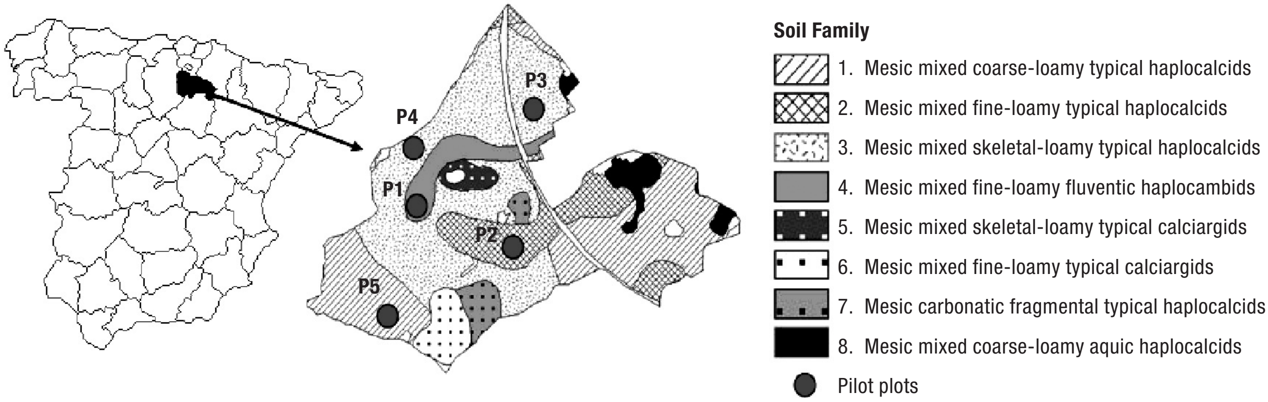


**Figure 1.** The location of the nitrate vulnerable zone (NVZ) of the Aldeanueva in the region of La Rioja (North Spain), and the soil map of the NZV at the family level, with the location of the pilot plots (circles).

of water were replaced with river water with a lower $NO_3^-$ concentration. The Tempranillo grape is the major variety grown in the area. Grapes are most commonly grown on trellises with N-S orientation, with 85% of the crop area drip-irrigated. Irrigation is usually applied according to crop demand but is limited by the regional normative and by GAP up to the time of veraison. The total annual irrigation usually does not exceed 150 mm.

The area contains eight main soil families, which are defined according to their parent material and shown on a 1:20,000 soil map (Gobierno de la Rioja, 2005) (Fig. 1). All of the soils are classified as Aridisols and belong to three subgroups: Haplocambids, Calciargids, and Haplocalcids (Soil Survey Staff, 1998). These represent 5, 6, and 84% of the agricultural area, respectively (Table 1). Soils in the top layer are alcaline (pH range between 8.0 and 8.3) and low in organic matter content (between 0.9 and 1.2 %). These soils are well structured and fairly porous, but differences in coarse fraction (including large gravel and stone content) and texture at the family level lead to differences in permeability.

Daily data on the maximum and minimum air temperature, air humidity, radiation, precipitation, and wind speed were obtained from the climatic station of Aldeanueva de Ebro located on the site (42° 13’ 15” N, 1° 54’ 23” W, 635 m height), from the *Servicio de Información Agroclimática de La Rioja.* From 2005 to 2007, the precipitation levels for each year were 423, 424, and 486 mm; the potential evapotranspiration levels by Penman-Monteith were 866, 825, and 796 mm; and the mean daily temperatures were 13.8, 14.8 and 14°C. Following Papadakis (1960), this climate corresponds to mild continental Mediterranean.

The production of organic manures in the area was estimated on the basis of livestock numbers at 52 Mg ha$^{-1}$ (equivalent to 312 kg N ha$^{-1}$). Most of the organic manure (90%) is currently exported out of the NVZ, while the rest is applied to the vineyard at a rate of approximately 10 Mg ha$^{-1}$ every two years (personal communication from *Centro de Investigación y Desarrollo Agrario de La Rioja*).

## Field data

The period of model validation extended from March 2005 to November 2007. Five pilot plots (monitoring fields between 0.7 and 2.8 ha) were maintained on the more relevant soil families of the study area (Fig. 1). Pilot plot P1 was located in soil type code 4, P2 was located in soil 2, P3 and P4 were located in soil 3, and P5 was located in soil 1. The four soil types covered 82.6% of the area. Each plot was established in a commercial vineyard (Tempranillo variety) and divided into three replications. Table 2 shows the main characteristics and management practices for each plot. Organic manure application varied from 0 to 24 Mg ha$^{-1}$ (equivalent to a range of 0-144 kg N ha$^{-1}$); the manure was incorporated into the soil after spreading. The water used for irrigation had a stable $NO_3^-$ concentration (1.7 mg N L$^{-1}$) and was taken directly from the river channel and applied by drip irrigation.

The soil samples were taken throughout the three years of the study, but most of the samples were taken during the growing season. The soil mineral nitrogen (SMN) and the soil water content (SWC) were determined from samples taken with an Eijkelkamp® helicoidal

**Table 1.** Percentage of the area occupied by each soil family in the nitrate vulnerable zone, and main soil characteristics used to define soil profiles in STICS: horizons, bulk density (BD), coarse fraction (CF), clay content, soil water content at field capacity (WFC), and soil water content at wilting point (WWP)

| Soil code | Family | Area (%) | Horizons (m) | OM (%) | BD (g cm$^{-3}$) | CF (%) | Clay (%) | WFC (mm) | WWP (mm) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Mesic mixed coarse-loamy typical haplocalcids | 27.3 | 0-0.37 | 0.54 | 1.4 | 2.5 | 12.3 | 24.9 | 10.8 |
| | | | 0.38-0.70 | 0.35 | 1.5 | 0.5 | | 28.1 | 13.3 |
| | | | 0.71-1.12 | 0.29 | 1.5 | 0.5 | | 28.3 | 13.4 |
| 2 | Mesic mixed fine-loamy typical haplocalcids | 12.7 | 0-0.37 | 0.96 | 1.4 | 0.5 | 21.7 | 34.5 | 20 |
| | | | 0.38-0.81 | 0.77 | 1.5 | 0.5 | | 33.7 | 19.4 |
| | | | 0.82-1.0.43 | 0.24 | 1.5 | 2.5 | | 24.9 | 10.8 |
| 3 | Mesic mixed skeletal-loamy typical haplocalcids | 37.5 | 0-0.38 | 0.87 | 1.4 | 2.5 | 22.9 | 34.3 | 19.9 |
| | | | 0.39-0.80 | 0.78 | 1.5 | 53 | | 33.8 | 19.6 |
| | | | 0.81-1.25 | 0.43 | 1.5 | 75 | | 22.5 | 8.8 |
| 4 | Mesic mixed fine-loamy fluventic haplocambids | 5.1 | 0-0.36 | 1.02 | 1.4 | 0.5 | 23.3 | 38.6 | 24.3 |
| | | | 0.37-0.87 | 1.08 | 1.5 | 0.5 | | 39.3 | 25.5 |
| | | | 0.88-1.40 | 1.01 | 1.5 | 0.5 | | 40.7 | 27.4 |
| 5 | Mesic mixed skeletal-loamy typical calciargids | 1.7 | 0-0.14 | 1.24 | 1.4 | 3.5 | 11.8 | 22.6 | 9.0 |
| | | | 0.15-0.30 | 0.74 | 1.5 | 10 | | 29.7 | 15.3 |
| | | | 0.31-0.40 | 0.45 | 1.5 | 27.5 | | 31.1 | 16.6 |
| 6 | Mesic mixed fine-loamy typical calciargids | 4.1 | 0-0.50 | 0.69 | 1.4 | 3.5 | 14.1 | 28.7 | 13.9 |
| | | | 0.51-0.90 | 0.89 | 1.5 | 10 | | 33.8 | 19.3 |
| | | | 0.91-1.60 | 0.71 | 1.5 | 85 | | 33.2 | 18.2 |
| 7 | Mesic carbonatic fragmental typical haplocalcids | 3.2 | 0-0.40 | 0.6 | 1.4 | 27.5 | 14.2 | 26.4 | 12.1 |
| | | | 0.41-0.85 | 0.86 | 1.5 | 80 | | 21.1 | 7.8 |
| | | | 0.86-1.70 | 0.86 | 1.5 | 80 | | 21.1 | 7.8 |
| 8 | Mesic mixed coarse-loamy aquic haplocalcids | 3.7 | 0-0.30 | 0.69 | 1.4 | 3.5 | 13.2 | 28.1 | 13.4 |
| | | | 0.31-0.58 | 0.65 | 1.5 | 10 | | 29.5 | 14.8 |
| | | | 0.59-0.97 | 0.19 | 1.5 | 27.5 | | 25.8 | 11.2 |

**Table 2.** Main features, crop management practices, monitoring period, and number of measurements of soil water content (SWC) and soil mineral nitrogen (SMN) for each pilot plot

| | P1 | P2 | P3 | P4 | P5 |
|---|---|---|---|---|---|
| *Plot description* | | | | | |
| Planting year | 1989 | 2002 | 1995 | 1997 | 1979 |
| Soil depth (cm) | 100 | 100 | 60 | 60 | 100 |
| Planting layout (m × m) | 2.8 × 1.2 | 2.6 × 1 | 2.8 × 1.2 | 2.8 × 1.2 | 2.25 × 1.2 |
| Monitoring period | 2005-2007 | 2005-2007 | 2006-2007 | 2006-2007 | 2006-2007 |
| *No. of measurements*[1] | | | | | |
| SWC | 51 | 51 | 36 | 36 | 36 |
| SMN | 51 | 51 | 36 | 36 | 36 |
| *Crop management practices* | | | | | |
| Organic manure (Mg ha$^{-1}$) | | | | | |
| 2007 | 0 | 24 | 15 | 0 | 0 |
| Irrigation (L m$^{-2}$) | | | | | |
| 2005 | 72 | 136 | — | — | — |
| 2006 | 83 | 50 | 53 | 61 | 40 |
| 2007 | 92 | 46 | 60 | 47 | 24 |

[1] No. of measurements equal number of sampling dates times replicates. —: no data (year without monitoring).

auger (1.7 cm i.d. by 15.5 cm long) at intervals of 0.2 m up to the maximum soil depth. Plots P1 and P2 were sampled 5, 5 and 7 times in 2005, 2006 and 2007, respectively; and plots P3, P4 and P5 were sampled 5 and 7 times in 2006 and 2007, respectively. SWC was measured gravimetrically. The samples needed for the SMN were extracted (1:5) with 1 M KCl, centrifuged, and stored in a freezer until later analysis. The ammonium and $NO_3^-$ concentrations of the soil extracts were determined by spectrophotometry using the Griess-Ilosvay and the indophenol methods, respectively (Keeney and Nelson, 1982). The total number of measurements is shown in Figure 2.

The grapes in the plots were harvested in the first two weeks of October. The total biomass, yield, and dry weight of the various aboveground plant parts (summer pruning, canes, leaves, and grapes) were determined for every plot and for each year. In each plot, each plant measurement was obtained as the average of ten plants. The fresh material was dried to a constant weight at 65°C. Subsamples were analyzed for their N concentration (AOAC, 1990). The crop nitrogen content for the various plant parts was calculated as the product of the biomass and the N concentration, and the nitrogen crop uptake (NCU) was obtained by summing the N content in the aboveground plant parts.

## Modeling

*Validation of N and water balances*

A modeling approach was adopted because $NO_3^-$ leaching cannot be measured at this scale using direct methods (lysimeters or drained perimeters). A standard crop-soil model that accounts for mineralization and transport of $NO_3^-$ through the soil profile relies on the SWC and SMN measurements to calculate the water and $NO_3^-$ fluxes. The crop-soil model STICS (Simulateur mulTIdisciplinaire pour les Cultures Standards) was selected because it allows for simulation of a wide range of agricultural practices that are common to vineyards and includes specific subroutines for grapevine development, growth and yield, as well as N and water balance in the plant-soil system. The core code is linked to plant files that define the specific features of various crops and their varieties. A detailed description of STICS can be found in Brisson *et al*. (2003). The specific simulation of the water and nitrogen balances can be found in Brisson *et al*. (2009). STICS

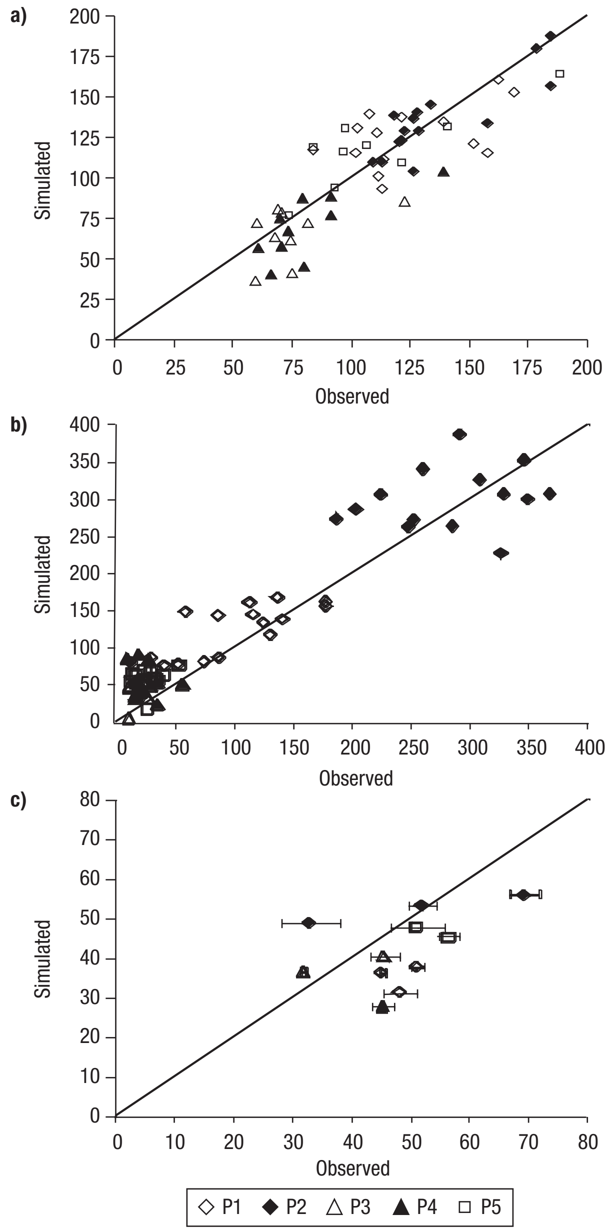


**Figure 2.** A comparison of the observed and simulated values for the pilot plots (P1 to P5) of soil water content (SWC, mm) (a), soil mineral nitrogen (SMN, kg N $ha^{-1}$) (b), and nitrogen crop uptake (NCU, kg N $ha^{-1}$) (c). Continuous lines show a 1:1 correlation. For NCU, the SDs of the observed values are indicated using horizontal lines.

has been calibrated to simulate the growth and development of various grape varieties cultivated in France (García de Cortázar, 2006). It has been also been calibrated for the Tempranillo variety, the major variety grown in the NVZ; the crop parameters used in our model were taken from the Tempranillo calibration (Ruiz-Ramos *et al*., 2009).

In this study, additional validation was performed focusing on the variables that are relevant to the levels of N and the water balances: in particular, SMN, SWC and NCU. This validation was done using field data from the pilot plots and climate data from a local meteorological station. The other model inputs that were necessary concern the soil characteristics, initial soil stage, and technical operations. A soil file for STICS was built from the characteristics of the soil families in each pilot plot (Fig. 1, Table 1). Field capacity and wilting point were estimated for all of the horizons based on texture and bulk density (Saxton *et al*., 1986). The main variables defining the initial state of the soil systems were SWC and SMN at the beginning of the simulation for each pilot plot. The technical files were built according to the observed practices of the pilot plots (Table 2). The crop residues were returned and incorporated into the top layer.

### *Model evaluation*

Evaluation of STICS performance focused on SMN, SWC and NCU, and followed the methodology proposed by Whitmore (1991) and Nash and Sutcliffe (1970). The statistics included the mean absolute error (MAE) between the measured and the simulated data, the root mean square error (RMSE), and the coefficient of efficiency (E). In general, improvement in model performance is characterized by a decrease in the MAE and the RMSE, given by [1] and [2]:

$$MAE = N^{-1} \sum_{i=1}^{N} |O_i - S_i| \qquad [1]$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N} (O_i - S_i)^2}{df}} \qquad [2]$$

where $N$ is the number of observations, $O_i$ represents the observed data, $S_i$ represents the simulated data, and $df$ is the calculated degrees of freedom of the residual sum of squares.

The coefficient of efficiency ranges from minus infinity to 1.0 (with greater values indicating better agreement) and is calculated as:

$$E = 1.0 - \frac{\sum_{i=1}^{N} (O_i - S_i)^2}{\sum_{i=1}^{N} (O_i - \bar{O})^2} \qquad [3]$$

where $\bar{O}$ is the mean of the observed values. The coefficient of efficiency is the ratio of the mean square error between the measured and the simulated data to the variance in the observed data subtracted from unity. Thus, a value of zero for E indicates that the model is as good a predictor as $\bar{O}$, whereas negative values indicate that $\bar{O}$ is a better predictor than the model.

## Simulation of nitrogen management scenarios

For this study, eight management scenarios were generated, combining two criteria: 1) four levels of organic manure application: no application (R0 treatments), 10 Mg ha$^{-1}$ equivalent to 60 kg N ha$^{-1}$ every two years (R1 treatments, representative of actual management in the NVZ), 28.3 Mg ha$^{-1}$ equivalent to 170 kg N ha$^{-1}$ [RN treatments, corresponding to the maximum annual dose of organic N permitted by the European normative (EC, 1991)], and 51.7 Mg ha$^{-1}$ equivalent to 331 kg N ha$^{-1}$ (RZ treatments, corresponding to the local use of all of the manure generated annually in the NVZ); and 2) two levels of $NO_3^-$ in the irrigation water: 1.7 mg N L$^{-1}$ (E treatments) corresponding to water drawn from the Ebro river, and 32.7 mg N L$^{-1}$ (P treatments) for the water pumped from the perched aquifer. The combinations were designated as: R0E, R0P, R1E, R1P, RNE, RNP, RZE and RZP. A technical file was built for each treatment. The N contribution is specified in Table 3.

The soil file was created to include the eight soil families present in the NVZ (Fig. 1, Table 1). The weather files were constructed using the weather generator ClimGen (Stöckle *et al*., 2001) by calculating a statis-

**Table 3.** Annual nitrogen application (via irrigation water or organic manure) of the simulated treatments

| Treatment code | Applied with irrigation water (kg N ha$^{-1}$) | Applied as organic manure (kg N ha$^{-1}$) |
|---|---|---|
| R0E | 2.5 | 0 |
| R0P | 49 | 0 |
| R1E | 2.5 | 60[1] |
| R1P | 49 | 60[1] |
| RNE | 2.5 | 170 |
| RNP | 49 | 170 |
| RZE | 2.5 | 312 |
| RZP | 49 | 312 |

[1] Every two years.

tically representative time series based on 30 years of historical data from the weather station. Simulations were run for a period of 22 years and to compare the effects of the various management practices, crop yield and biomass were selected to test crop performance. CNU, SMN after harvest, drainage, and $NO_3^-$ leaching were used to test the water and N balances.

The study area was divided into homogeneous units with respect to the soil types, and the STICS model was applied to each unit. The model was linked to a GIS (ArcGIS v. 9.2, ESRI, 2006), allowing for spatial analysis of the output variables suited to the detection of trends and differences in response to crop management and soil type. Maps were constructed to consider the effects of the different management practices on each variable relative to the R0P treatment. This treatment combined a zero application of organic N and irrigation with polluted water from the aquifer: the characteristics of management used in the recent past. The total $NO_3^-$ leached from the NVZ was calculated for each scenario by combining the $NO_3^-$ leaching rate and the surface area for each soil family. Actual contribution to the aquifer was calculated as the balance between leaching and N extracted for irrigation.

All simulations were conducted under the same irrigation regime, which provided a total annual application of 150 mm with five applications before veraison. The simulations were run with the same crop parameters than in the validation process.

# Results

## Validation of N and water balances

The STICS model was able to reproduce, with adequate accuracy, the SWC and SMN measured at the five pilot plots at different times during the three study years, in response to the soil variability (Fig. 2). The simulated mean of SWC was 109.3 mm, close to the observed mean of 112.3 mm (MAE = 15 mm). The broad range observed in SWC values, which ranged from 60 mm in dry periods to 190 mm in wet periods, was properly simulated for the different pilot plots (RMSE = 18.9 mm). The simulated mean of SMN was 127.3 kg N ha$^{-1}$, close to the observed mean of 101.7 kg N ha$^{-1}$ (MAE = 36 kg N ha$^{-1}$). The broad range observed in SMN values (high for P2, medium for P1, and low for the rest) was properly simulated (RMSE = 44.2 kg N ha$^{-1}$). The observed mean CNU was 47.9 kg N ha$^{-1}$ and was comparable to the simulated mean of 42 kg N ha$^{-1}$ (RMSE = 11.4 kg N ha$^{-1}$). The mean values were correctly simulated, although slightly underestimated for plots P1 and P4. This underestimation could lead to an overestimation of SMN.

The strongest agreement between observed and simulated values was seen for SMN; this variable obtained the highest E value, although the E values for all variables were close to 1. Only the observed mean for CNU was a better estimator than the model because of the negative value of E; however, this value was not far from zero, indicating only a small difference in predictive ability. The RMSE and MAE values appeared in the same order, showing that the outliers were not relevant in these datasets. These results allow the application of the model to simulate drainage and nitrate leaching in the area with confidence.

## Scenario analysis

The simulations show the effect of the local climate variability on the temporal evolution of the variables. As an example, Figure 3 shows the simulation results for the soil occupying most of the surface in the NVZ (soil 3), the cycles of SMN accumulation and $NO_3^-$ leaching are related to the precipitation pattern. Dry periods are characterized by SMN accumulation, whereas wet years lead to large $NO_3^-$ leaching. Nitrate leaching estimations in the first year depended of the initial conditions and this influence disappeared after 13 years of simulation. After this period, the simulations allowed for identifying a five-year period that captured weather variability (Fig. 3). Considering these facts, all of the results below refer to the period representing years 18-22 of the simulations. To consider the effects of the various management practices, the mean results from this period were compared across treatments.

### *Soil mineral nitrogen*

SMN levels varied greatly with treatment. In the example shown in Figure 3b after year 13, the treatments that combined low application of manure and irrigation with river water (R0E, R1E) stabilized around SMN = 90 kg N ha$^{-1}$. The treatments that received a large application of N (either from manure or from irrigation water) showed peaks of SMN accumulation but later stabilized. For soil 3, the mean SMN in the last five simulation years for RZP was 400 kg N

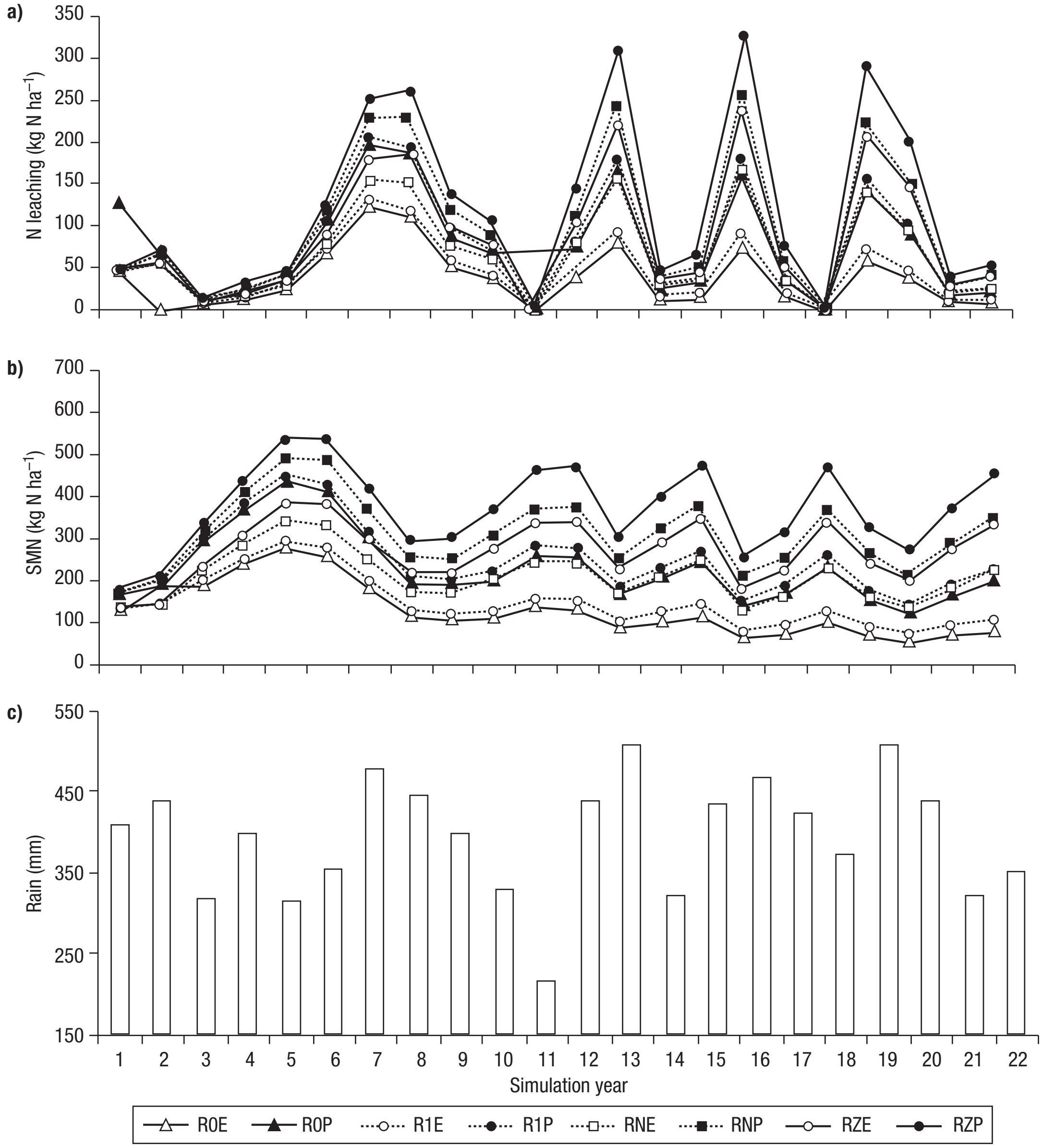


**Figure 3.** Simulation of nitrate leaching (a), and soil mineral nitrogen (b) time course in soil 3 for the eight treatments considered in the study, and annual rainfall (c).

ha$^{-1}$; for RNP and RZE, the mean was 300 kg N ha$^{-1}$. Similar patterns were observed in the other soils, but the SMN values were greatly dependent on soil type. The lowest values of SMN across the NVZ were obtained for soil 1, for which treatment R0E stabilized at SMN = 50 kg N ha$^{-1}$. Soils 2 and 4, which had medium clay content, presented SMN greater than 800 kg N ha$^{-1}$ for the treatment with RZP.

Average values of SMN in the last five simulation years are shown in Table 4a for each treatment. Maps presenting the relative values of the tested variables are also an appropriate tool for analyzing various scenarios. Compared to the R0P reference scenario, the E scenarios showed a reduction in SMN of up to 100% over the entire NVZ (Fig. 4a,b,c) except for the RZE treatment, for which a reduction in the SMN only appeared in half of the NVZ (Fig. 4d). The simulations also showed dramatic differences between the P and E scenarios. All of the P treatments showed an increase in the SMN compared to the R0P (Fig. 4e,f,g).

The individual soils also behaved very differently. Soils 1, 5, 6, 7 and 8 responded in a similar way with

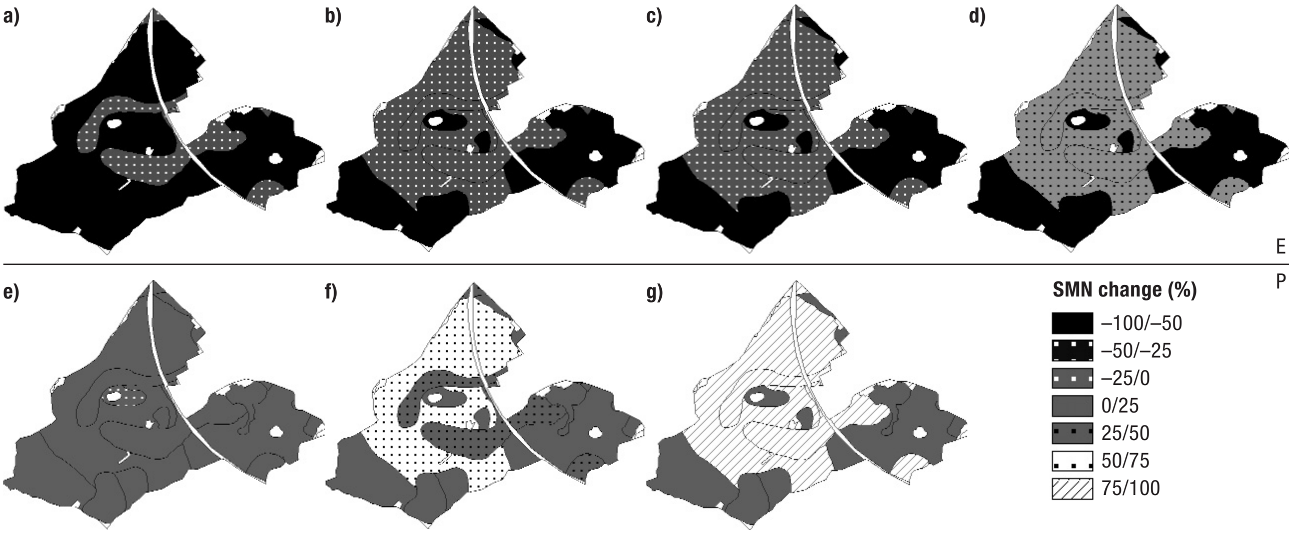


**Figure 4.** Maps of the change in SMN in the NVZ for treatments R0E (a), R1E (b) RNE (c), RZE (d), R1P (e), RNP (f), and RZP (g) expressed as the percentage of SMN under R0P treatment. The solid line separates the P and E treatments.

respect to R0P, showing a decrease or small increase in SMN. All of these soils had low clay content. In particular, soil 7 had a high coarse fraction and soil 5 was very shallow; these properties diminished SMN accumulation. Soils 2, 3 and 4, which had medium clay content, were more sensitive to treatments; whereas the application of low N caused a 50% reduction in SMN, the application of a large amount of N as manure or irrigation water led to an increase of 100% in SMN (Fig. 4).

*Drainage*

The annual drainage was similar for all simulations, independent of treatment. The model produced different responses depending on soil type, with values ranging between 25 and 75 mm per year in 80% of the NVZ (Fig. 5 shows an example for years 18-22 of the R1E treatment simulations). The minimum simulated drainage values were found for soils with a medium clay content (soils 2, 3 and 4, with drainage levels of approximately 20 mm), whereas the maximum values of approximately 100-115 mm corresponded to soil 7, which had a low clay content and a high coarse fraction. Soil 5, which was very shallow and had low clay content, also had a high drainage rate. Soils 1, 6 and 8 displayed intermediate drainage due to their combination of features: soil 1 had a low coarse fraction and a low clay content, and soils 6 and 8 had low coarse fractions that increased with depth as well as low clay content (Table 1).

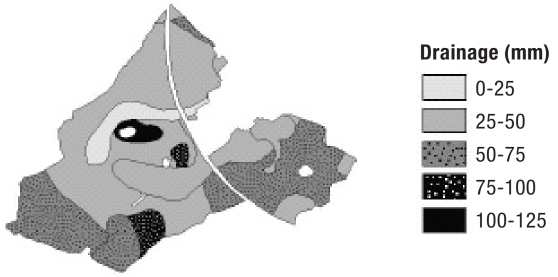


**Figure 5.** Simulated drainage in the nitrate vulnerable zone (NVZ) under the R1E treatment.

## Nitrate leaching

Nitrate leaching ranged between 2 and approximately 100 kg N ha$^{-1}$, depending on treatment and soil (Table 4b); values were larger in the soils with medium clay content (2, 3 and 4). Nitrate leaching in soils 2, 3, and 4 represented at least 70% of total $NO_3^-$ leaching across the NVZ for all treatments (Table 4c). Soil 3 (which represented 38.6% of cultivated area) was responsible for the greatest leaching. Soil 6 contributed to the smallest $NO_3^-$ leaching per area, although few differences were found between the values for soils 1, 6, 7 and 8 (Table 4b). All of these soils have low clay content, with a low coarse fraction at a depth of at least 40-60 cm.

The treatments can be clustered according to $NO_3^-$ leaching: R0E and R1E showed the lowest values and

**Table 4.** Soil mineral nitrogen (SMN) per treatment (a), simulated nitrate leaching per hectare (b), and total amount of nitrate leaching from the area occupied by each soil type, nitrate leaching from the whole nitrate vulnerable zone (NVZ) for each treatment and per year, and actual contribution of $N\text{-}NO_3^-$ to the aquifer (c)

| Soil | Treatment | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **R0E** | **R0P** | **R1E** | **R1P** | **RNE** | **RNP** | **RZE** | **RZP** |
| a) *SMN (kg $N\text{-}NO_3^-$ $ha^{-1}$)* | | | | | | | | |
| | 139.26 | 319.08 | 159.7 | 340.55 | 253.25 | 434.96 | 351.87 | 533.24 |
| b) *Nitrate leaching (kg $N\text{-}NO_3^-$ $ha^{-1}$)* | | | | | | | | |
| 1 | 4.2 | 31.6 | 4.3 | 31.6 | 4.6 | 32.0 | 4.5 | 32.8 |
| 2 | 37.3 | 62.4 | 40.6 | 65.8 | 57.2 | 82.8 | 74.8 | 101.6 |
| 3 | 22.4 | 50.2 | 27.4 | 55.6 | 50.8 | 80.2 | 75.4 | 105.8 |
| 4 | 28.5 | 44.4 | 29.9 | 46.0 | 39.2 | 55.4 | 51.5 | 68.2 |
| 5 | 9.3 | 44.0 | 9.3 | 44.0 | 9.6 | 44.8 | 9.5 | 45.2 |
| 6 | 2.4 | 27.4 | 2.4 | 26.2 | 2.8 | 28.4 | 2.6 | 28.6 |
| 7 | 3.6 | 37.6 | 3.7 | 37.6 | 3.8 | 38.4 | 3.7 | 39.2 |
| 8 | 4.5 | 29.8 | 4.6 | 29.8 | 4.8 | 30.8 | 4.9 | 31.6 |
| c) *Nitrate leaching (Mg $N\text{-}NO_3^-$)* | | | | | | | | |
| 1 | 0.99 | 7.48 | 1.02 | 7.48 | 1.09 | 7.58 | 1.06 | 7.77 |
| 2 | 4.11 | 6.88 | 4.48 | 7.26 | 6.31 | 9.13 | 8.25 | 11.21 |
| 3 | 7.30 | 16.36 | 8.93 | 18.11 | 16.55 | 26.13 | 24.56 | 34.47 |
| 4 | 1.25 | 1.95 | 1.31 | 2.02 | 1.72 | 2.43 | 2.26 | 2.99 |
| 5 | 0.13 | 0.63 | 0.13 | 0.63 | 0.14 | 0.65 | 0.14 | 0.65 |
| 6 | 0.08 | 0.98 | 0.09 | 0.93 | 0.10 | 1.01 | 0.09 | 1.02 |
| 7 | 0.10 | 1.04 | 0.10 | 1.04 | 0.11 | 1.07 | 0.10 | 1.09 |
| 8 | 0.15 | 0.96 | 0.15 | 0.96 | 0.16 | 1.00 | 0.16 | 1.02 |
| Total NZV | 14.12 | 36.29 | 16.21 | 38.45 | 26.17 | 48.99 | 36.62 | 60.21 |
| Actual contribution | 14.12 | –4.21 | 16.21 | –2.05 | 26.17 | 8.49 | 36.62 | 19.71 |

RNE presented an intermediate value, while the cluster comprised of R0P, R1P and RZE and the cluster with RNP and RZP produced the greatest $NO_3^-$ leaching. However, when the actual nitrate contribution to the aquifer in P treatments was computed, only balances for RNE and RZE were over the annual 20 Mg N $yr^{-1}$ delivered to the river from the aquifer (Zeta Amaltea, 2005), contributing to underground water pollution (Table 4c).

Compared to the R0P reference scenario, the E scenarios showed a reduction of up to 100% in the $NO_3^-$ leaching for cluster R0E-R1E (Fig. 6a,b), whereas there was a reduction in only about half of the NVZ for the RNE and RZE treatments (Fig. 6c,d). Simulations also showed dramatic differences between scenarios P and E. All of the P treatments showed an increase in $NO_3^-$ leaching compared to the R0P (Fig. 6e,f,g), whereas the soils under the E treatments responded differently to the levels of organic manure application. Soils 1, 5, 6, 7 and 8 responded in a similar way, showing a decrease or a small increase in $NO_3^-$ leaching with respect to R0P, as was found for SMN. Soils 2, 3 and 4, which had medium clay content, were again more sensitive to treatment. A reduction in $NO_3^-$ leaching for all soils occurred in the cluster R0E-R1E, and only for soils 2 and 4 under RNE (Fig. 6). In these soils, the application of a large amount of N in the manure or through the use of irrigation water led to large increases in $NO_3^-$ leaching (over 100% with respect to the R0P in treatments with the largest application rates) (Fig. 6).

### *Crop outputs*

The outputs related to the crop variables were obtained for the entire NVZ, revealing a narrow range of variation for all scenarios. The absolute values of CNU were between 40-62 kg N $ha^{-1}$, with the most variability linked to soil type rather than treatment. Variations in

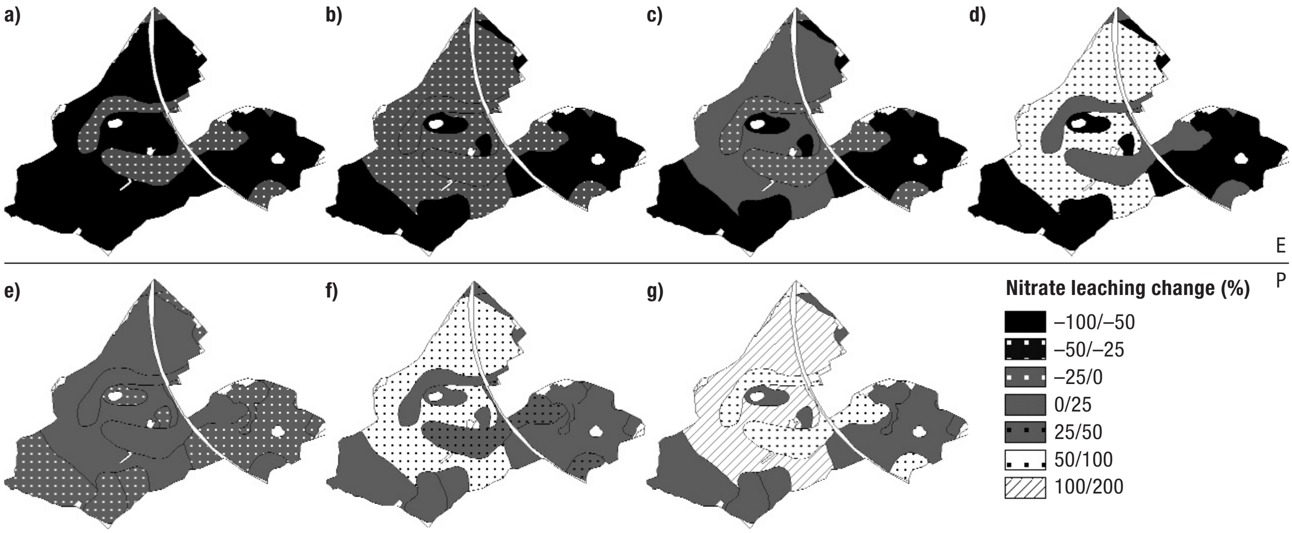


**Figure 6.** Maps of the nitrate leaching changes in the NVZ for treatments R0E (a), R1E (b) RNE (c), RZE (d), R1P (e), RNP (f), and RZP (g) expressed as the percentage of nitrate leaching under the R0P treatment. The solid line separates the P and E treatments.

the yield (from 10 to 15 Mg ha$^{-1}$) and dry biomass (from 5.5 to 7.5 Mg ha$^{-1}$) were due to the treatment (less than 5%) and the soil type (accounted for less than 15%). Most of the variation occurred from year to year.

## Discussion

The model was able to reproduce well the differences in SMN among the different soil types, although was not accurate simulating the different crop cycles within each soil. SMN of the pilot plots was properly simulated for values greater than 100 kg N ha$^{-1}$, establishing the capability of the model to identify soils with a high $NO_3^-$ potential risk. Lower SMN values revealed overprediction, particularly at the end of the crop cycle, but these cases were linked to low $NO_3^-$ leaching, and their relative influence on the total $NO_3^-$ leached from the NVZ was small. The observed and simulated values of CNU in the application study were within the range of 20-70 kg N ha$^{-1}$ reported by Champagnol (1984). Measurements of CNU were taken at harvest; the slight underestimation for certain pilot plots was probably related to the previously indicated overprediction of SMN. Overall, the validation supported the capacity of the model to simulate water and N balances.

As expected, the simulated values of drainage in the scenario analysis were small, as evapotranspiration greatly exceeds precipitation in the NVZ and irrigation was limited. The simulated values of SMN were high and in agreement with other studies performed in the Ebro Valley: Vázquez *et al*. (2005) reported approximately 450 kg N ha$^{-1}$ in 1 m of soil at the beginning of the growing season for loamy soils, and Abad *et al*. (2003) reported up to 900 kg N ha$^{-1}$ in 0.9 m for a clay loam soil. The simulated values for R1E were also consistent with the results obtained in the pilot plots established in our study area that followed a similar management plan. All of the points in Figure 2b showing SMN levels between 100 and 400 kg N ha$^{-1}$ corresponded to plots P1 and P2 (soils 4 and 2, respectively; Fig. 1), although SMN was slightly overestimated. The SMN measurements corresponding to plots P3, P4 (soil 3) and P5 (soil 1) were below 100 kg N ha$^{-1}$. Soils 2 and 4 presented the lowest drainage (Fig. 3) and a high exchange capacity; therefore, a high N leaching potential was expected (Follet *et al*., 1991). Soil 3, which covered 38% of the NVZ, presented an intermediate and sensitive response to SMN depending on the treatment (Fig. 2), which is understandable because this soil combines medium clay content with a high coarse fraction. The different responses seen for SMN due to soil type in treatments P and E were mainly due to the high exchange capacity of clay soils and the high ammonia volatilization losses simulated by the STICS model in soils with low clay content. The effect of soil texture on ammonia volatilization losses has been widely reported, and large volatilization has been observed in soils with a large coarse fraction and a low exchange capacity (Meisinger and Randall, 1991).

The $NO_3^-$ leaching per area was greatest in soils 2, 3 and 4, and contributed to approximately 75% of the NVZ leaching. Soil 3 was especially important because of its area and sensitivity to management and because it presented the highest $NO_3^-$ leaching under high N application. This result can be explained by the combination of medium clay content and an increasing coarse fraction with increasing depth. The importance of the coarse fraction of the soil to the $NO_3^-$ leaching was stressed by Delgado *et al*. (1994) using the NLEAP model. In soils with a high coarse fraction, soil mineral N concentration tends to increase in the soil matrix and is easily leached when drainage occurs. Our results agree with Vázquez *et al*. (2006), who reported that even soils with medium or low drainage might have high $NO_3^-$ leaching potential; SMN tends to increase in dry periods in these cases, and when drainage occurs, the leachate is high in $NO_3^-$. These findings show that differences in the $NO_3^-$ leaching of NVZ soils depend more on the ability of these soils to store N than on their differences in terms of annual drainage.

Even if the $NO_3^-$ leaching results mentioned above are relevant, care should be taken when considering the absolute values simulated by the model. Limitations linked to direct measurement of nitrate leaching implied that validation had to be focused in SWC and SMN; therefore errors of nitrate leaching estimates were not available. It was already mentioned that in soils 2 and 4 SMN was overestimated, so probably an overestimation of the $NO_3^-$ leaching could be expected as well. Besides, the high gaseous losses simulated by STICS avoid large SMN accumulation in treatments with high organic manure application, and therefore lessen differences in $NO_3^-$ leaching between treatments. The importance of gaseous losses in N balance is well known and reported in the literature, particularly in agricultural soils treated with large organic N applications (Meisinger and Randall, 1991).

Considering that the current vineyard management in the NVZ is very close to R1E, long-term simulation of $NO_3^-$ leaching for this scenario suggests that the current pollution problem is not caused by current management practices, but rather is a consequence of poor agricultural practices during previous decades. Vineyards that have progressively replaced horticultural crops are low input and offer opportunities for land and water reclamation in vulnerable areas if properly managed. In other studies performed in the Ebro valley, $NO_3^-$ leaching in horticultural crops ranged from 80 to 233 kg N ha$^{-1}$ for loamy soils, depending on SMN and irrigation management (Vázquez *et al*., 2005). In the intensive agricultural region of eastern Spain, $NO_3^-$ leaching reached 450 kg N ha$^{-1}$ due to irrigation with groundwater high in $NO_3^-$ concentration, accounting for one of the major N inputs in the area (Ramos *et al*., 2002).

The simulated values of the plant-related variables in the scenario analysis were not sensitive to treatment, including values of NCU, which were always within the range reported by Champagnol (1984). Therefore, the interest of using a well-calibrated crop model relies on simulating the uptake of N throughout the crop development cycle, and its interaction with SMN. Both NCU and SMN are key variables in determining the potential risk for $NO_3^-$ leaching (Follet *et al*., 1991).

The mass balance of $NO_3^-$ in the aquifer excludes the treatments with high level of organic manure and water from Ebro River. Practices incorporating all of the residues (RZE scenario) would aggravate the contamination problem in both soil and water. Practices conducted according to the EU directive (RNE) would reduce $NO_3^-$ leaching and SMN in half of the NVZ, but the organic manure application should be adjusted to each specific soil type. This scenario would require exporting approximately 50% of the local organic residues, and including high N demand crops in agricultural systems, because regional normative ("Programa de actuación", BOR, 2009) currently limits to 50 kg ha$^{-1}$ the total N that can be applied to vineyards. Although P treatments would have positive effects on the aquifer, they contribute to high risk for water pollution as they always increase the SMN up to 100% with respect to the reference treatment (Fig. 4e,f,g). Actually, all P treatments always were above 300 kg N-$NO_3^-$ ha$^{-1}$, and when combined with high level of organic manure above 400 kg N-$NO_3^-$ ha$^{-1}$ (Table 4a). Besides, a high SMN is well known to produce a low grape quality (Keller and Hrazdina, 1998; Bell and Hens, 2005). Therefore, the P treatments would lead to diminish aquifer pollution at the expense of a high risk for water pollution and reducing grape quality. Also, as in the NVZ vineyard evpotranspitarion is usually larger than precipitation, P treatments would lead to an increase of [$NO_3^-$] in the aquifer. On the contrary, adding water from the Ebro River would have a dilution effect. The treatments R0E and R1E presented a combination of total nitrate leaching below the threshold of 20 Mg N-$NO_3^-$ yr$^{-1}$, a decrease in SMN between 25 and 100% (Fig. 4a,b), and low SMN (below 160 kg N-$NO_3^-$ ha$^{-1}$, Table 4a). These treatments would lead to an improvement of aquifer pollution, but at a slower rate than treatments R0P and R1P. Current practices (R1E) might help to reduce the N pollution problem locally, but require the exportation of most of the organic residues generated in the NVZ.

Therefore, water pollution and future risk due to high SMN were driven by both the $NO_3^-$ concentration of irrigation water and the level of organic manure application. Special attention should be paid to soils 2, 3, and 4, because their responses to treatments were very different. According to these results, good agricultural practices (GAP) are proposed as follows: i) use only water from the Ebro river for irrigation if vineyard is maintained; ii) limit the application of organic manure to 60 kg N ha$^{-1}$ every two years for non-selective application types; and iii) increase the application of organic manure up to 170 kg N ha$^{-1}$ with the following constraints: 1) conducting selective management of manures based on the soil type (applications to soils 2, 3 and 4 should be limited to 60 kg N ha$^{-1}$ every two years), 2) include high N demand crops in the systems following limitations in the "Programa de actuación" of the La Rioja Government (BOR, 2009).

The GAP proposed would result in surplus organic manure in the NVZ. Within a regional planning context, possible options are: i) reducing organic manure production in the NVZ, ii) composting the majority of organic residues, and iii) exporting the residues (as is currently practiced). The last option should be studied carefully to ensure that only organic residues are being exported, not the pollution problem.

## Conclusions

This work improved the understanding of the driving processes causing $NO_3^-$ pollution in a representative NVZ of irrigated vineyards in Mediterranean Europe. Differences in the $NO_3^-$ leaching of the NVZ soils depend more on their ability to store N than on their differences in annual drainage. In soils with medium clay content and large coarse fraction, soil mineral N concentration tends to increase in the soil matrix during dry periods and is then easily leached when drainage occurs. High SMN and water pollution was driven by both the $NO_3^-$ concentration of irrigation water and the level of organic manure application. The use of aquifer water for irrigation would lead to diminish aquifer pollution at the expense of maintaining high SMN, non desirable for grape quality production. However, river water offers an opportunity for the recovery of soils and the improvement of underground water quality if the application of organic manure is limited. For this reason, manure application needs to be adjusted to match the proposed recommendations. These recommendations are feasible and easy to implement, as they clarify the origin and remedy of the pollution problem. In any case, good agricultural practices should be adapted to soil type. Further simulations could help to identify more accurately a threshold level of organic residue application for soils with an intermediate response.

The long term simulation of current crop practices in the NVZ revealed that the pollution problem is not related to the current management regime, but rather is a consequence of poor agricultural practices during previous decades, including the overwatering of crops with water from the aquifer. Both the new management practice and the GAP proposed for $NO_3^-$ pollution control would result in surplus organic manure in the NVZ. Regional planning is needed to attend to the excess manure.

## Acknowledgments

This work was supported by the *Centro de Investigación y Desarrollo Tecnológico Agroalimentario,* CIDA (Gobierno de la Rioja). In particular, we thank A. Pardo, M.J. Suso, and L. Olasolo from CIDA. We would also like to thank David Connor for his valuable comments and help with the manuscript.

## References

ABAD A., LLOVERAS J., MICHELENA A., 2003. Nitrogen fertilization and foliar urea effects on durum wheat yield and quality and on residual soil nitrate in irrigated Mediterranean conditions. Field Crop Res 87, 257-266.

AOAC, 1990. Official methods of analysis, 15th ed. Association of Official Analytical Chemist, Washington, USA.

BEAUDOIN N., LAUNAY M., SAUBOUA E., PONSARDIN G., MARY B., 2008. Evaluation of the soil crop model STICS over 8 years against the "on farm" database of Bruyères catchment. Eur J Agron 29, 46-57.

BOR, 2009. Decree 79/2009, of 18 December, that modifies the designation of Vulnerable Zones, including a new vulnerable zone, the Najerilla low alluvial, and approves the New Action Program, Agronomic Measurements, and Sampling of Vulnerable Zones to pollution from agricultural origin. Boletín Oficial de La Rioja [In Spanish].

BRISSON N., GARY C., JUSTES E., ROCHE R., MARY B., RIPOCHE D., ZIMMER D., SIERRA J., BERTUZZI

P., BURGER P. *et al.,* 2003. An overview of the crop model STICS. Eur J Agron 18, 309-332.

BRISSON N., LAUNAY M., MARY B., BEAUDOIN N. (eds), 2009. Conceptual basis, formalisations and parameterization of the STICS crop model. QUAE, Paris, France. 304 pp.

CHAMPAGNOL F., 1984. Eléments de physiologie de la vigne et de viticulture générale. Saint-Gely-du-Fesc, France. 351 pp. [In French].

DELGADO J.A., FOLLET R.F., SHARKOFF J.L., BRODAHL M.K., SHAFFER M.J., 1994. NLEAP facts about nitrogen management. J Soil Water Conserv 53, 332-337.

DE PAZ J.M., RAMOS C., 2004. Simulation of nitrate leaching for different nitrogen fertilization rates in a region of Valencia (Spain) using a GIS-GLEAMS system. Agr Ecosyst Environ 103, 59-73.

EC, 1991. Council directive of 12th December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources (91/676/EEC). Official Journal of the European Union 30/12/91 L135/1 to 8.

EC, 2000. Council directive of 23th October 2000 establishing a framework for Community action in the field of water policy (2000/60/EC). Official Journal of the European Union 22/12/2000 L327/1 to 73.

ESRI, 2006. ArcGIS software v.9.2. ESRI Inc, 1999-2006.

FOLLET R.F., KEENEY D.R., CRUSE R.M., 1991. Managing nitrogen for groundwater quality and farm profitability. Soil Science Society of America, Madison, USA. 357 pp.

GARCÍA DE CORTAZAR I., 2006. Adaptation du modèle STICS à la vigne (*Vitis vinifera* L.). Utilisation dans le cadre d'une étude d'impact du changement climatique à l'échelle de la France. Doctoral thesis. École Nationale Supérieure Agronomique, Montpellier, France. [In French].

GOBIERNO DE LA RIOJA, 2005. Mapa de suelos de Aldeanueva de Ebro escala 1:20.000. Consejería de Agricultura y Desarrollo Rural. Logroño, Spain. [In Spanish].

KEENEY D.R., NELSON D.W., 1982. Nitrogen-inorganic forms. In: Methods of analysis, Part 2. Chemical methods (Page A.L., ed). American Society of Agronomy and Soil Science Society of America, Madison, USA. pp. 643-698.

LEDOUX E., GÓMEZ E., MONGET J.M., VIAVATTENE C., VIENNOT P., DUCHARNE A., BENOIT M., MIGNOLET C., SCHOTT C., MARY B., 2007. Agriculture and groundwater nitrate contamination in the Seine basin. The STICS-MODCOU modelling chain. Sci Total Env 375, 33-47.

MAPA, 2001. Yearbook of Agricultural Statics [on-line]. Ministerio de Agricultura, Pesca y Alimentación, Madrid. Available in http://www.mapa.es/es/estadistica/ infoestand.htlm [29 April 2009]. [In Spanish].

MEISINGER J.J., RANDALL G.W., 1991. Estimating nitrogen budgets for soil crop systems. In: Managing nitrogen for groundwater quality and farm profitability. Soil Science Society of America, Madison, USA. pp. 84-124.

MMA, 2004. Las aguas continentales en la Unión Europea. Centro de publicaciones de la Secretaría General Técnica del Ministerio del Medio Ambiente, Madrid, Spain. [In Spanish].

NASH J.E., SUTCLIFFE J.V., 1970. River flow forecasting through conceptual models, Part I - A discussion of principles. J Hydrol 10, 282-290.

PAPADAKIS J., 1960. Geografía agrícola mundial. Ed Salvat, Barcelona, Spain. 648 pp. [In Spanish]

RAMOS C., AGUT A., LIDÓN A., 2002. Nitrate leaching in important crops of the Valencian Comunity region (Spain). Environ Pollut 118, 215-223.

RUIZ-RAMOS M., GABRIEL J.L., VÁZQUEZ N., QUEMADA M., 2009. Calibration and validation of STICS-vigne for the variety Tempranillo in the region of Rioja (Spain). Proc 16th Nitrogen Workshop - Connecting different scales of nitrogen use in agriculture. Turin, Italy, June 28-July 1. pp. 493-494.

SAXTON K.E., RAWLS W.J., ROMBERGER J.S., PAPENDICK R.I., 1986. Estimating generalized soil water characteristics from texture. T ASAE 50, 1031-1035.

SOIL SURVEY STAFF, 1998. Keys to soil taxonomy, 8th ed. USDA Natural Resource Conservation Service, Washington DC, USA. 644 pp.

STÖCKLE C.O., NELSON R., 1994. Cropping systems simulation model: user's online manual. Washington State University. Pullman, USA. 132 pp.

STÖCKLE C.O., NELSON R.L., DONATELLI M., CASTELLVÌ F., 2001. ClimGen: a flexible weather generation program. Proc 2nd Int Symp Modelling Cropping Systems. Florence, Italy, July 16-18. pp. 229-230.

TRABADA-CRENDE F., VINTEN J.A., 1998. Assessing the effects of land management and catchment hydrology on well water quality in a designated nitrate vulnerable zone. Agr Syst 57, 523-540.

TSUJI G., UEHARA G., BALAS S. (eds), 1994. DSSAT version 3. International Berchmark Sites Network for Agrotechnology Transfer, University of Hawaii, Honolulu, USA. 164 pp.

VÁZQUEZ N., PARDO A., SUSO M.L., QUEMADA M., 2005. A methodology for measuring drainage and nitrate leaching in unevenly irrigated vegetable crops. Plant Soil 269, 297-308.

VÁZQUEZ N., PARDO A., SUSO M.L., QUEMADA M., 2006. Drainage and nitrate leaching under processing tomato growth with drip irrigation and plastic mulching. Agr Ecosyst Env 112, 313-323.

WHITMORE A.P., 1991. A method for assessing the goodness of computer simulation of soil processes. J Soil Sci 42, 289-299.

ZETA AMALTEA, 2005. Estudio de afección de los nitratos procedentes de la agricultura a los acuíferos de La Rioja y delimitación de zonas vulnerables. Technical report for the Confederación Hidrográfica del Ebro, Zaragoza, Spain. 50 pp. [In Spanish].