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Using RZWQM to simulate the fate of nitrogen in field soil–crop environment in the Mediterranean region

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ABSTRACT

This paper presents an evaluation of the root zone water quality model (RZWQM) for assessing the fate of N in the soil–crop environment at the field scale in Portugal under two distinct agricultural systems; one consists of a grain corn planted in a silty loam soil with level basins (flood) irrigation and the other a forage corn planted in a sandy soil with sprinkler irrigation. Water balance and crop growth were reported in a previous study [Cameira, M.R., Fernando, R.M., Ahuja, L., Pereira, L.S., 2005. Simulating the fate of water in field soil–crop environment. J. Hydrol. 315, 1–24] using RZWQM. This study reports RZWQM simulated nitrogen transformation, uptake and transport in the two soil–crop systems with emphasis on the calibration of the soil organic matter pools and selected soil N transformation processes (mineralization, hydrolysis and nitrification), using 2 years of data (1996 and 1997). The criterion for model calibration was that the root mean square error (RMSE) of the simulations was lower than the average standard deviation of measured data (MSD) for the simulation period. A third year (1998) was used to validate the model performance under four different fertilization management practices. Predicted corn grain yield was within 1.1% of measured values. The error varied between −10 and 2.4% for forage corn. N uptake was predicted with an error of 2.8% for grain corn and between −13 and −3% for forage corn. For the silty loam soil and during the crop season, nitrate-N in the soil profile was predicted with a RMSE lower than the MSD. For the sandy soil, RMSE was lower than MSD for one fertilizer treatment and slightly higher for the other two treatments. The prediction of the residual nitrate-N in the soil, after crop harvest, presented errors ranging from 18 to 37%. The results show that the model was able to predict N related variables for the two soil–crop systems and for the different boundary conditions (irrigation and fertilization) with a good accuracy.

1. Introduction

Non-point source pollution is a leading cause for water quality problems but, due to its dispersed nature, it cannot be monitored directly in the same manner as point source pollutions. The need to quantify the fates of nitrogen from rural regions under various conditions of climate, soils, water management, cropping pattern and agricultural technologies has increased. These quantifications will help identify the best management practices (BMP) to minimize N leaching losses while maintaining crop yields. Simulation models can rapidly make long-term analyses as opposed to expensive and time-consuming classical field research. A range of potential BMPs can be evaluated using models, and the most promising ones

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can be field tested. Model results can be used in conjunction with field demonstration sites to help the development of BMP's for the farms. But before using the models as management tools, we must ensure that models and their parameters are evaluated as much rigorously as possible. In order to collect appropriate data for evaluation, the experiments need to be properly designed since the accuracy of model predictions cannot exceed the accuracy of the input data used in the analysis. Since some parameters often cannot be measured directly or easily, they must be derived by fitting to data, independent of the type of the problem to be simulated (Addiscot et al., 1995). Once a suitable model has been developed and tested, long-term simulation studies and interpolation of results between field research stations are possible. In addition, knowledge gaps concerning whole system and subsystem interactions can be identified for further study.

Many models are available today to simulate the fate of water and N in the soil–crop environment. In this context the root zone water quality model (RZWQM) is unique in its major emphasis on simulating the effects of main agricultural management practices on soil–water–plant processes that influence water and N in soils. RZWQM is an agricultural system model developed over the past 15 years by USDA-ARS, Agricultural Systems Research Unit in Fort Collins, in cooperation with several other scientists (Ahuja et al., 2000). It integrates the state-of-the-science knowledge of agricultural systems into a tool for agricultural research and management, environmental assessment, and technology transfer. The primary use of RZWQM is as a tool for assessing the environmental impact of alternative management strategies on a field-by-field basis and predicting management effects on crop production.

The reliability of any model depends on how well each individual process is represented in the model and on the accuracy of the measured parameters needed to run the model. The main RZWQM components have undergone extensive verification, evaluation and refinement in collaboration with several users in the USA. These components are water movement (Ahuja et al., 1993, 1995), pesticide transport (Ahuja et al., 1993, 1996), evapotranspiration (Farahani et al., 1996; Farahani and Ahuja, 1996; Alves and Cameira, 2002), subsurface tile drainage (Johnsen et al., 1995; Singh et al., 1996), organic matter/nitrogen cycling (Ma et al., 1998), and plant growth (Nokes et al., 1996; Ma et al., 2000).

There are significant interactions among different components of the system. To achieve acceptable simulation results for nitrate transport, good descriptions of soil water fluxes, crop growth and N uptake are required. Also, to properly simulate the water balance components, a good description of crop development and root growth is needed, since they determine evapotranspiration and water uptake. So it is not possible to evaluate the nitrogen component without evaluating the crop and hydrology component of the model.

In Portugal, the studies with RZWQM started in 1993, aiming to obtain a tool to analyze the impacts of alternative irrigation and fertilization practices upon the groundwater quality and crop production. Two major objectives were defined: (1) evaluate the model capability to predict soil water and N related processes in an irrigated crop for different conditions in relation to: (i) soils; (ii) crop varieties; (iii) irrigation practices (method, frequency and amounts); (iv) fertilization practices (type of fertilizer, frequency of application and amounts); (2) develop a calibration methodology and verify its adequacy. The objectives for the water related processes were dealt and accomplished in a previous paper (Cameira et al., 2005). This paper reports the procedure used to parameterize the N transformations and the capability of the model to predict N uptake, storage in the soil and transport in two soil–crop systems, with different irrigation and fertilization practices.

2. RZWQM overview

As a system model, RZWQM includes several components or modules aiming to describe a complete agricultural system. Each subsystem is illustrated in detail in several publications, e.g. Ahuja et al. (2000). In this paper we will focus on the components of interest for the present study.

2.1. *Nitrogen transformations*

The organic matter and nitrogen (OMNI) module in RZWQM was developed to simulate soil carbon and nitrogen transformations. OMINI is a state-of-the art model for carbon (C) and nitrogen (N) cycling in soil systems (Shaffer et al., 2001). It simulates the major pathways of the soil carbon–nitrogen dynamics including mineralization–immobilization of crop residues, manure and other organic wastes, mineralization of the soil humus fraction, inter-pool transfers of carbon and nitrogen, denitrification, ammonia volatilization and nitrification. The C/N cycling is affected by management practices such as irrigation, tillage, manure application and fertilization.

Organic matter (OM) is distributed over five computational pools and decomposed by three microbial mass populations (BM). The OM pools consist of slow and fast pools for crop residues, and fast, medium and slow pools for soil humus. The fast and medium soil OM pools correspond to the potentially mineralizable N pool. These five pools are dynamically linked together as shown in Fig. 1. The fast residue pool has a C:N ratio of 80, and the slow one has a C:N ratio of 8, modified to account for manure (Ma et al., 1998). Partitioning of fresh residues between the fast and the slow residue pools is based on the C:N ratio and N mass balance. The three organic matter pools have C:N ratios of 8 (fast), 10 (intermediate) and 12 (slow), respectively. In addition, there are three types of soil microorganisms: aerobic heterotrophs, autotrophs and facultative heterotrophs. All three microbial pools have a C:N ratio of eight (Shaffer et al., 2001).

For all the pools, the basic form of the decay rate equations for organic matter differs only by the values of the user-supplied rate coefficients. The equations are all first order with respect to the carbon substrate source (Shaffer et al., 2001). The general rate equation is of the form:

$$r_{\mathrm{dec,i}} = -K_{\mathrm{dec,i}} C_{\mathrm{i}} \tag{1}$$

where $r_{\mathrm{dec,i}}$ is the decay rate (μg g soil^{-1} day^{-1}), i the organic matter pool index ($1 < i < 5$), C_{i} the carbon substrate

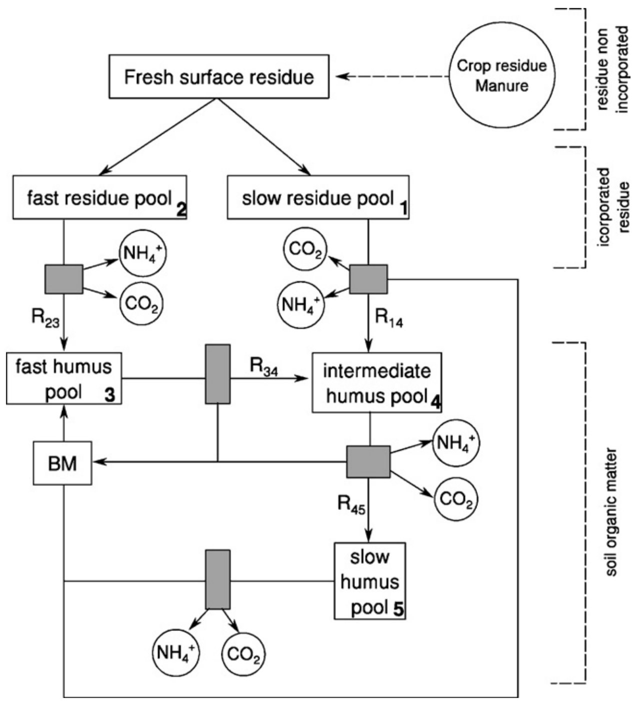

Fig. 1 – A schematic diagram of residue and soil organic matter pools in RZWQM. R_{14}, R_{23}, R_{34} and R_{45} are inter-pool mass transfer coefficients and BM is microbial biomass (modified form Ma et al., 1998).

concentration (μg g soil^{-1}) and k_{dec} is the first order rate coefficient (day^{-1}), which is a function of the soil environment variables like O_2 and H concentrations, soil temperature and a pool-specific rate coefficient, A_i (day^{-1} organism^{-1}) (model data base or user supplied).

Obtained model parameters associated with soil carbon decay result in a turnover time of 5, 20 and 2000 years for the fast, intermediate and slow humus pools, respectively. Parameters related to surface residue pools were calibrated from corn residue data (Shaffer et al., 2001). A fraction of decayed organic materials is transferred between pools as denoted by R_{14}, R_{23}, R_{34} and R_{45} in Fig. 1. A set of R values ($R_{14} = 0.6$, $R_{23} = 0.1$, $R_{34} = 0.1$ and $R_{45} = 0.1$) was calibrated by Ma et al. (1998) based upon an experimental study in a corn field, and is used in the model. Because the C:N rations are different among pools, nitrogen conservation is observed during the transformations. The model uses CO_2 as a carbon sink or source without keeping a balance of it in the model.

Nitrogen is released as inorganic NH_4^+, during the decay process and may be nitrified to NO_3^- by autotrophic bacteria, following a zero order equation:

$$r_{nit0} = -K0_{nit} \tag{2}$$

where r_{nit0} is the zero order nitrification rate (moles NH_4^+ L_{PW}^{-1} day^{-1}), where L_{PW} means liters of pore water; $K0_{nit}$ the zero order rate coefficient for nitrification (moles NH_4^+ L_{PW}^{-1} day^{-1}), function of the autotrophic biomass population (no. of organisms g^{-1} soil) and the nitrification rate coefficient, A_{nit} (day^{-1} organism^{-1}) (data base or user defined).

Nitrate from nitrification or applied commercial fertilizers is subject to denitrification under anaerobic conditions, and the denitrification rate is described using a first order equation:

$$r_{den} = -K_{den} C_{NO_3} \tag{3}$$

where C_{NO_3} in the NO_3^- concentration in soil solution (moles NO_3^- L_{PW}^{-1}); K_{den} the first order denitrification rate (moles NO_3^- L_{PW}^{-1} day^{-1}), function of the carbon substrate concentration (μg C g^{-1} soil), the anaerobic microbe biomass (no. of organisms g^{-1} soil) and the denitrification rate coefficient, A_{den} (day^{-1} organism^{-1}) (data base or user defined).

Urea from applied commercial fertilizers is hydrolyzed to NH_4^+ as a first order equation:

$$r_u = -K_u C_{urea} \tag{4}$$

where r_u is the hydrolysis rate of urea (moles urea L_{PW}^{-1} day^{-1}); C_{urea} the urea concentration (moles L_{PW}^{-1}) and K_u is the first order coefficient for urea hydrolysis (day^{-1}), calculated by the model, as a function of soil temperature and a rate coefficient, A_u (day^{-1}) (model data base or user supplied).

Ammonia volatilization is modeled based on partial pressure gradient of NH_3 in the soil (P_{NH_3}) and air (P'_{NH_3}):

$$r_v = -K_v T_f (P_{NH_3} - P'_{NH_3}) C_{NH_4} \tag{5}$$

where K_v is a volatilization constant, affected by wind speed and soil depth; T_f a temperature factor; C_{NH_4} is the NH_4 concentration in the soil.

A detailed description of the processes and calculations is given by Ma et al. (2000). The model was thoroughly tested for mass balance (Shaffer et al., 2000; Hanson, 2000; Ma et al., 1998). This component is complex and it may be difficult to determine the input parameters. The required inputs are then determined through an initialization wizard and calibration as discussed below.

2.2. Nitrogen uptake and partitioning in the plant

The amount of N that passively enters the plant is determined by the N associated with the transpiration stream in the plant. If passive N uptake is unable to satisfy plant N demand, the active uptake occurs in a manner similar to the Michaelis–Menten substrate model (Hanson, 2000). Plant N demand of each organ (leaf, root, stem, seed) is calculated from daily growth of each organ and N needed to maintain a certain N concentration in the organ. Roots have first access to available nitrogen. Subsequently, all remaining N is hierarchically allocated to other plant organs. Propagule N demand is met first when the plants are in the reproductive stage. If N is still available the remaining is partitioned in the proportion of the demand by leaves and stems. For maize, the model also allows for N uptake above N demand using a luxurious uptake factor. The excessive N uptake above N demand is stored in a separate pool and is used to meet N demand when N uptake is limited (Hanson, 2000; Ma et al., 2000).

2.3. *Soil nitrogen movement*

Nitrogen transport occurs both in the soil matrix and in the macropores. The soil matrix is divided into micropore (immobile soil solution) and mesopore (mobile soil solution) zones, which introduces a form of preferential flow transport in the soil matrix. Microporosity is based on either input values or soil water content at 2000 cm suction. Initially and during the first wetting of a 1 cm increment, soil water and chemicals in meso- and micropores are in equilibrium. During successive infiltration steps the miscible displacement of solution in the saturated soil layers occurs only in the mesopores, thus changing the soil solution concentration. After infiltration, the nitrate in the meso- and micropores is instantaneously equilibrated.

Then diffusion occurs between meso- and micropores solutions and the concentrations in each region are appropriately adjusted. The equation for the diffusion process is

$$\frac{\Delta C_{\mathrm{sol}}}{\Delta t} = D_{\mathrm{a}}(C_{\mathrm{micr}} - C_{\mathrm{sol}}) \tag{6}$$

where C_{sol} is the concentration of chemical in solution in the mesopores (mg $\mathrm{L^{-1}}$); C_{micr} the concentration in solution of the micropores (mg $\mathrm{L^{-1}}$) and D_{a} is the apparent diffusion coefficient/diffusion distance factor ($\mathrm{h^{-1}}$) (model data base or user defined). D_{a} is calculated as:

$$D_{\mathrm{a}} = D\xi \tag{7}$$

where D is the solute diffusion coefficient in pure water and ξ is the tortuosity of the media. ξ is a function of the geometry (texture and structure) and the soil water content. One means to calculate ξ is given by Jury et al. (1991):

$$\xi = \frac{\theta^{3.3}}{\phi^{2}} \tag{8}$$

where θ is the soil water content ($\mathrm{cm^3\,cm^{-3}}$) and ϕ is the soil porosity ($\mathrm{cm^3\,cm^{-3}}$).

During water redistribution between rainfall or irrigation events, chemicals in solution move with water flux from one depth to another, including upward movement due to evaporation. The effect of preferential flow on nitrate transport is allowed by using a two-domain approach, the soil matrix and the macropores. The result is that the simulated solute transport undergoes a form of rapid mechanical dispersion associated with the preferential flow through the macropores (Ahuja et al., 1995).

Nitrate-N leached from the crop root zone, $L_{\mathrm{NO_3\text{-}N}}$ (mg $\mathrm{cm^{-2}}$), is computed by combining an estimate of nitrate-N dissolved in the soil pore water with estimates of soil water flux (Eq. (9)). The effects of soil macropores on nitrate-N leaching are included:

$$L_{\mathrm{NO_3\text{-}N}} = \varphi_{\mathrm{rz}} C_{\mathrm{NO_3\text{-}N}} \tag{9}$$

where φ_{rz} is the drainage flux at the bottom of the root zone (L $\mathrm{cm^{-2}}$), $C_{\mathrm{NO_3\text{-}N}}$ is the nitrate concentration in the pore water at the bottom of the root zone (mg $\mathrm{L^{-1}}$). More details are given in Ahuja et al. (2000).

3. Materials and methods

3.1. *Experimental fields*

The experiments were conducted during the years of 1996, 1997 (model calibration data) and 1998 (model validation data) in two 1-ha plots in an experimental station at Coruche, located in the Sorraia watershed in the South of Portugal. The climate is Mediterranean with an average annual rainfall (1950–1980) of 706 mm. Most of the rain occurs between October and May. Summers are hot and dry. The soil in one of the plots was a deep silty loam Eutric Fluvisol (FAO classification), often flooded during winter, with poor internal drainage, and having a water retention capacity (calculated as the storage at field capacity minus the storage at wilting point for a depth of one meter of soil) of 236 mm/m. During the crop cycle, the water table depth varies between 50 cm (May) and 180 cm (October). The soil in the other plot was a sandy Eutric Cambisol (FAO classification) with good drainage but low water retention capacity (103 mm/m). The water table was more than 500 cm deep not influencing the water dynamics in the root zone. Tables 1 and 2 list some measured physical and chemical properties of both soils.

Table 1 – Selected measured physical properties of the soils in the experimental plots

Depth (cm)	Particle size (%)				Bulk density	θ_{v} (%)			
	Coarse sand	Fine sand	Silt	Clay		2 kPa	10 kPa	32 kPa	1500 kPa
Silty loam soil (Eutric Fluvisol)									
0–25	1.5	54.2	27.9	16.4	1.43	39.9	36.6	33.1	11.4
25–50	1.4	53.8	28.0	16.8	1.55	39.7	36.0	32.2	12.4
50–80	1.6	56.1	25.2	17.1	1.58	38.2	35.1	33.5	12.3
Sandy soil (Eutric Cambisol)									
0–15	76.9	15.7	5.2	2.2	1.41	24.5	14.6	9.8	2.5
15–30	59.6	31.8	6.7	1.9	1.54	26.9	13.96	9.7	2.9
30–60	67.4	25.0	5.1	2.5	1.50	18.8	10.6	7.2	1.6

θ_{v} = volumetric soil water content.

Table 2 – Selected measured chemical properties of the soils in the experimental plots

Depth (cm)	pH	Organic matter			
		OM (%)	C_{org} (%)	N_{org} (%)	C/N
Silty loam soil (Eutric Fluvisol)					
0–25	6.5	1.26	0.73	0.10	7.3
25–50	7.1	0.98	0.57	0.078	7.3
50–80	7.9	0.47	0.28	0.041	6.7
Sandy soil (Eutric Cambisol)					
0–15	5.4	0.922	0.535	0.071	7.5
15–30	5.8	1.338	0.776	0.079	9.7
30–60	6.3	0.229	0.169	0.027	6.3

OM = organic matter, C_{org} = organic carbon and N_{org} = organic nitrogen.

Grain corn (FAO 600) and forage corn (FAO 200) were planted in the silty loam and sandy soils, respectively, for many years under current Sorraia Watershed management practices as described in Cameira et al. (2003). Irrigations and fertilizations were performed according to the farmer's normal practices. Grain corn was irrigated by the level basin (flood) method. During the 1996 season, seven irrigation events were performed with a total amount of 350 mm water applied. A total amount of 430 mm water was applied to forage corn, during the 1997 season, with 13 sprinkler irrigations. Fig. 2 shows precipitation, irrigations and crop evaporation for both systems during the calibration years. Crop evapotranspiration was calculated by the soil–plant daily water balance as described in Cameira et al. (2005). During the 1998 season, the validation year, a total amount of 395 mm was applied to grain corn and a total amount of 320 mm was applied to forage corn (Fig. 3). Fertilization treatments for the three experimental years and the two crop systems are shown in Table 3. Since the sandy soil/forage corn system presents favorable conditions for the occurrence of deep drainage and N Leaching, three different fertilization treatments were defined for model validation.

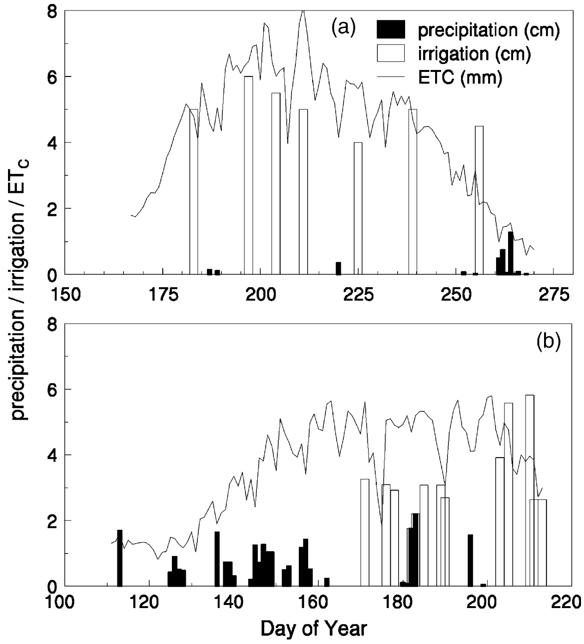

Fig. 2 – Precipitation, irrigations and crop evapotranspiration during the calibration years: (a) 1996 crop season (grain corn); (b) 1997 crop season (forage corn).

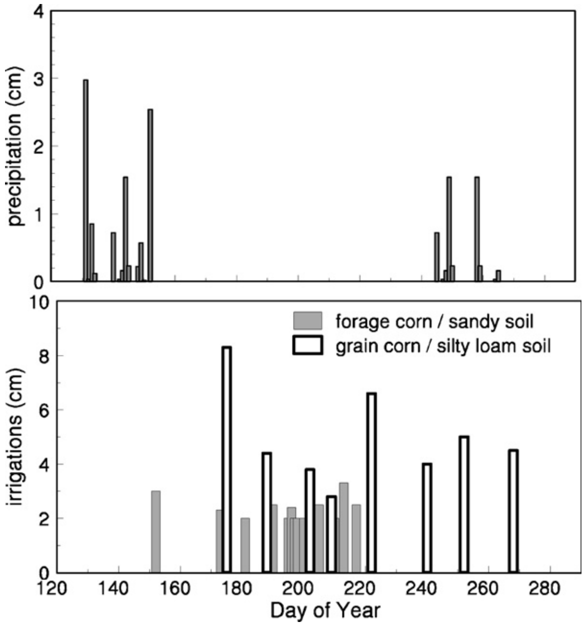

Fig. 3 – Precipitation and irrigations for the 1998 season, validation year.

3.2. Field measurements

Measurements regarding meteorological data, soil hydraulic properties, crop development and water balance were described in Cameira et al. (2003, 2005). In each plot three replicate sub-plots, each one with an area of 10 m^2, were isolated so that all the inputs could be carefully quantified. All the measurements related to water, nitrogen and plants were performed in these sub-plots.

3.2.1. *Model calibration data*

Field monitoring of the variables related to the water and N balance started in May 1996 for the silty loam plot and in April 1997 for the sandy plot. Before crop planting, nine soil samples were collected in each control area to characterize soil organic matter and the inorganic soil N ($N\text{-}NO_3$ and $N\text{-}NH_4$) pools. The samples were collected using a 150 cm long and 5 cm diameter auger, in a 1.3 m × 1.3 m grid and at the depths of 0–7.5, 7.5–22.5, 22.5–37.5, 37.5–52.5, 52.5–67.5 and 67.5–82.5 cm. The samples were stored in plastic bags and frozen until analysis. Organic carbon was determined using the dry combustion method (Tiessen and Moir, 1993). Organic matter was calculated multiplying organic carbon by a factor of 1.724 (Tiessen and Moir, 1993). Total soil N was determined by using the micro-Kjeldhal digestion followed by steam distillation (McGill and Figueiredo, 1993). NO_3-N and NH_4-N were extracted from the soil using a 2.3 M KCl solution. The concentration was measured using the segmented flux method (Maynard and Kalra, 1993). Organic N was determined

Table 3 – Fertilization treatments during calibration (1996 and 1997) and validation experiments (1998)

Application date	N amount (kg ha^{-1})	N form
Calibration experiments		
Silty loam soil (1996 season)		
Seeding (broadcast incorporated) (DoY 144)	42	Ammonium
4–8 leaves (irrigation water) (DoY 182)	120	UAN
Flowering (irrigation water) (DoY 256)	55	UAN
Sandy soil (1997 season)		
Seeding (broadcast incorporated) (DOY 104)	42	Ammonium
4–8 leaves (broadcast incorporated) (DOY 148)	150	Urea
Before flowering (broadcast incorporated) (DOY 173)	150	Urea
Validation experiments		
Silty loam soil (1998 season)		
Seeding (broadcast incorporated) (DoY 125)	42	Ammonium
4–8 leaves (irrigation water) (DoY 159)	200	Urea
Sandy soil (1998 season)		
Treatment A		
Seeding (broadcast incorporated) (DoY109)	72	Ammonium
4–8 leaves (broadcast incorporated) (DoY 146)	400	Urea
Treatment B		
Seeding (broadcast incorporated) (DoY 109)	72	Ammonium
4–8 leaves (broadcast incorporated) (DoY 146)	200	Urea
Treatment C		
Seeding (broadcast incorporated) (DoY 109)	72	Ammonium
4–8 leaves (broadcast incorporated) (DoY 146)	100	Urea

DoY: day of year, urea (46% N), UAN (50% urea + 25% NH_4-N + 25% NO_3-N).

subtracting the mineral nitrogen (NO_3^- + NH_4^+) from the total soil N.

During the crop growing season, soil samples were collected before and after each fertilization and the days after the irrigations at the same depths and places to monitor NO_3-N and NH_4-N. The samples were stored in plastic bags and frozen until analysis using the segmented flux method (Maynard and Kalra, 1993). At the same time samples from the irrigation water were collected and stored in plastic bottles and frozen until analysis.

Plant samples were collected for crop characterization (Cameira et al., 2003), and sub-samples were taken to evaluate-N in the different plant parts (leaves, stalks and grain) and hence the crop N uptake as described in Jones et al. (1991). The plant samples were cleaned, dried and weighted. Total N was determined using the Kjeldhal method (Bremner, 1979).

To estimate soil net mineralization, a very simplified experiment was performed. Three sub-plots with an area of 9 m^2, unplanted and unfertilized were isolated in each plot. These plots were not irrigated and the surface was protected from precipitation to prevent N leaching losses. During 4 months, soil samples were collected at the depths of 0–7.5, 7.5–22.5, 22.5–37.5, 37.5–52.5, 52.5–67.5 and 67.5–82.5 cm in the silty loam plot and at 7.5, 22.5 and 45 cm in the sandy plot, to determine the evolution of NO_3-N and NH_4-N concentrations. In each sub-plot nine samples were taken at each depth and date.

3.2.2. *Model validation data*

To obtain data for model validation the collection of soil and plant samples for nitrogen measurements and crop yield was repeated during the 1998 crop season for both systems.

3.3. *Data analysis—nitrogen balance*

Soil N balance was conducted for the plot scale using a simplified form of the nitrogen balance equation for the entire crop growth season from 5 May to 15 October for the silty loam soil, and from 14 April to 5 August for the sandy soil. The top system boundary was the canopy and the bottom boundary was the maximum rooting depth. The equation is written as (Meisinger and Randall, 1991):

$$A_{IN} + N_F + N_{IR} + N_{NM} = A_{FN} + N_{UT} + L_N \qquad (10)$$

where A_{IN} and A_{FN} are the mineral N storage at the beginning and at the end of the period, respectively, calculated from the mineral N concentrations measured in the soil samples; N_F the mineral N applied as fertilizer; N_{IR} the mineral N present in the irrigation water, calculated multiplying the volume of water applied during each irrigation by the mineral N concentration of the irrigation water; N_{UT} the mineral N uptake by the crop calculated multiplying the N concentration measured in the plants samples by the plant biomass; L_N the leached mineral N, determined by multiplying the drainage flux (Cameira et al., 2005) by the mineral N concentration in the soil solution at the bottom layer (Eq. (9)). This method does not consider the diffusion term of the transport equation but as it was shown by Kengni et al. (1994) this term represents at most only 6% of the convective term; N_{NM} the mineral N resulting from net mineralization of the organic matter, including the immobilization by soil microbes. Net N mineralization was estimated by analyzing the simultaneous variations of NO_3-N and NH_4-N storage in the profile during the 4-month experiment, as described in Section 4.

All terms are expressed in kg N ha^{-1}. The terms relative to gaseous N losses (volatilization and denitrification) were not considered because existing conditions do not favor volatilization and denitrification, with exception for the short periods after irrigation, in the silty loam soil, when water ponding at the soil surface can favor denitrification.

3.4. *Model calibration and validation procedures*

RZWQM requires a detailed set of parameters. Some of these parameters cannot be easily measured or determined. Variability with respect to model input data was recognized as a potentially significant source of uncertainty in model predictions (Rafsgaard et al., 1999). Kumar et al. (1999) related the discrepancies between measured and RZWQM simulated water and nitrates contents to the lack of calibration of the plant growth component. This is because in RZWQM, water and nutrient balance are a function of the crop growth and development. Therefore, an iterative calibration approach, involving the soil, plant growth, crop evapotranspiration and nutrient modules, is needed to account for the interactions among soil water, available nitrogen and crop production. After the calibration of each model component the simulations of the previous components were checked if necessary. The flow chart describing this methodology is presented in Fig. 4. The iterative approach reduces the error propagation between model components. The detailed calibration and validation for the hydrologic and plant sub models was presented in Cameira et al. (2005). This paper presents the detailed description of the nitrogen module calibration. However, as an iterative methodology was used, the results presented in this paper related with N uptake, leaching and

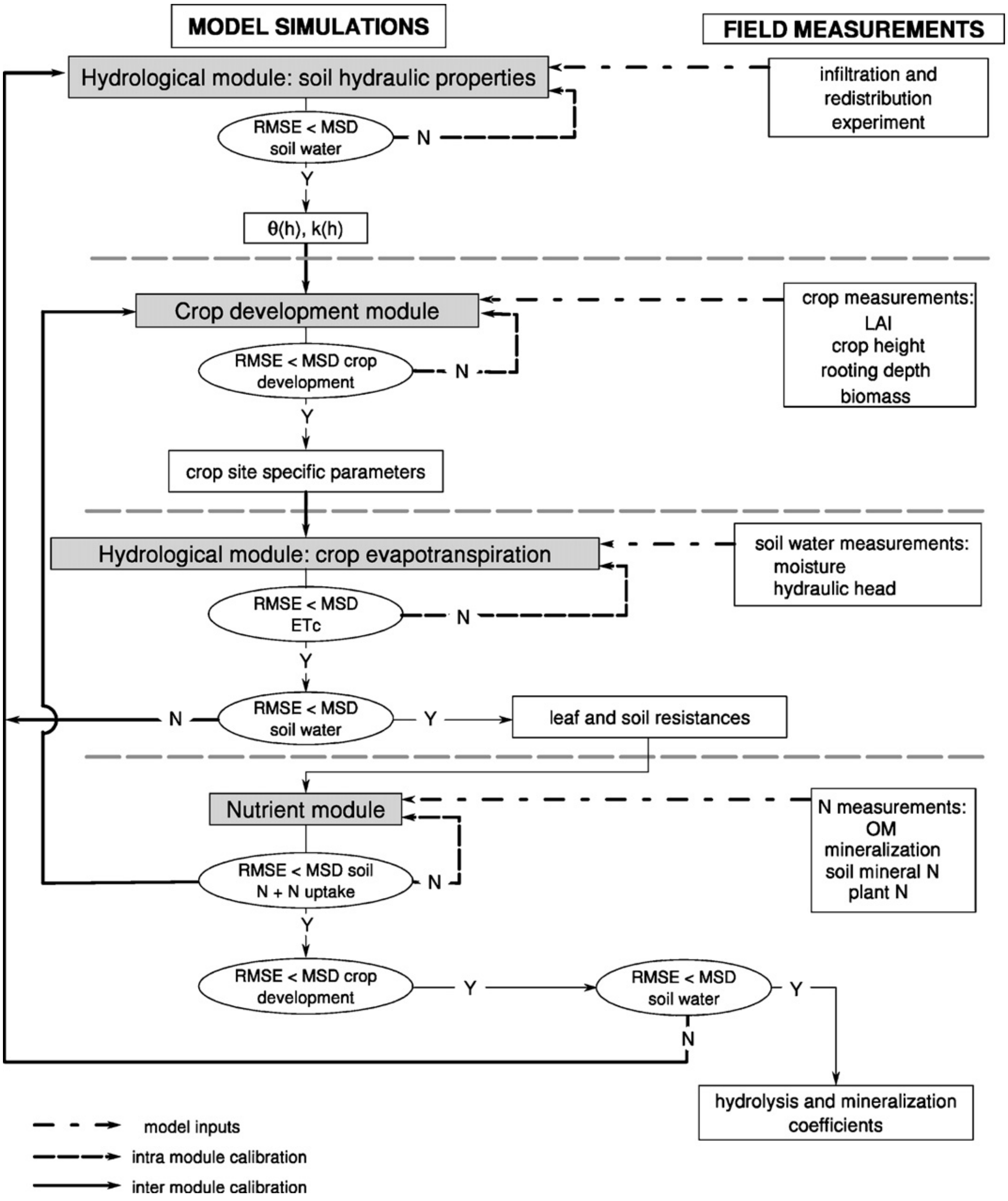

Fig. 4 – Flow chart describing the overall iterative calibration process of RZWQM.

storage in the soil were obtained after the calibration of all the modules, including the ones not presented in this paper.

The model was calibrated for the silty loam and the sandy soil using experimental data from 1996 and 1997, respectively. Two years' data were used for calibration because experiments were conducted on two different soils with two different crop varieties. The different model components were considered calibrated when the root mean square error (RMSE) of the simulations were lower than the mean standard deviation (MSD) of the measured data. The output variables used to control the calibration were N uptake by the crop and NO_3-N storage in the soil during the crop cycle. RMSE and MSD were calculated as

$$\mathrm{RMSE} = \left(\frac{\sum_{k=1}^{n}(S_k - O_k)^2}{n}\right)^{0.5} \tag{11}$$

$$\mathrm{MSD} = \frac{\sum_{k=1}^{n}\mathrm{SD}_k}{n} \tag{12}$$

where S_k are the simulated values, O_k are the observed values, n the number of measurements and SD_k is the standard deviation of measured values. Calibration on the nutrient model was performed in three steps (Fig. 5):

(i) Initialize SOM and MBM pools:

The initialization of these pools was performed following the model developers recommendations (Shaffer et al., 2001). Using the measured soil organic matter (SOM) per layer, the model estimates the initial microorganism pools based upon the conversion factors (950 for aerobic heterotrophs and 9500 for anaerobic heterotrophs and autotrophs). Soil OC in each layer is partitioned between the fast/transition soil humus pools and the stable soil humus pool. The authors recommend assuming that 5–40% of the OC is in the faster pools, and 95–60% is in the stable pool. We used a 5/95 proportion. Then the amount of available OC in each layer is partitioned between the fast and transition pools. This split is based upon the management history of the site. Soils with significant recent applications of animal manures and/or green manures would be expected to have a higher proportion of OC in the fast pool. Soils not receiving these amendments probably have a somewhat depleted fast pool. In this particular case no manure has been applied so 10% is assigned to the fast pools and 90% to the medium pool.

(ii) Equilibrate the pools

After the initialization of the soil OC, a 10-year simulation was performed for continuous maize crop using average weather conditions and management practices in order to obtain a stabilized fraction of the five pools of organic matter and the three pools of microorganisms. At the end of this period, if the simulated total SOM in the soil was similar to the observed one, while the rate of N mineralization was of the same order of

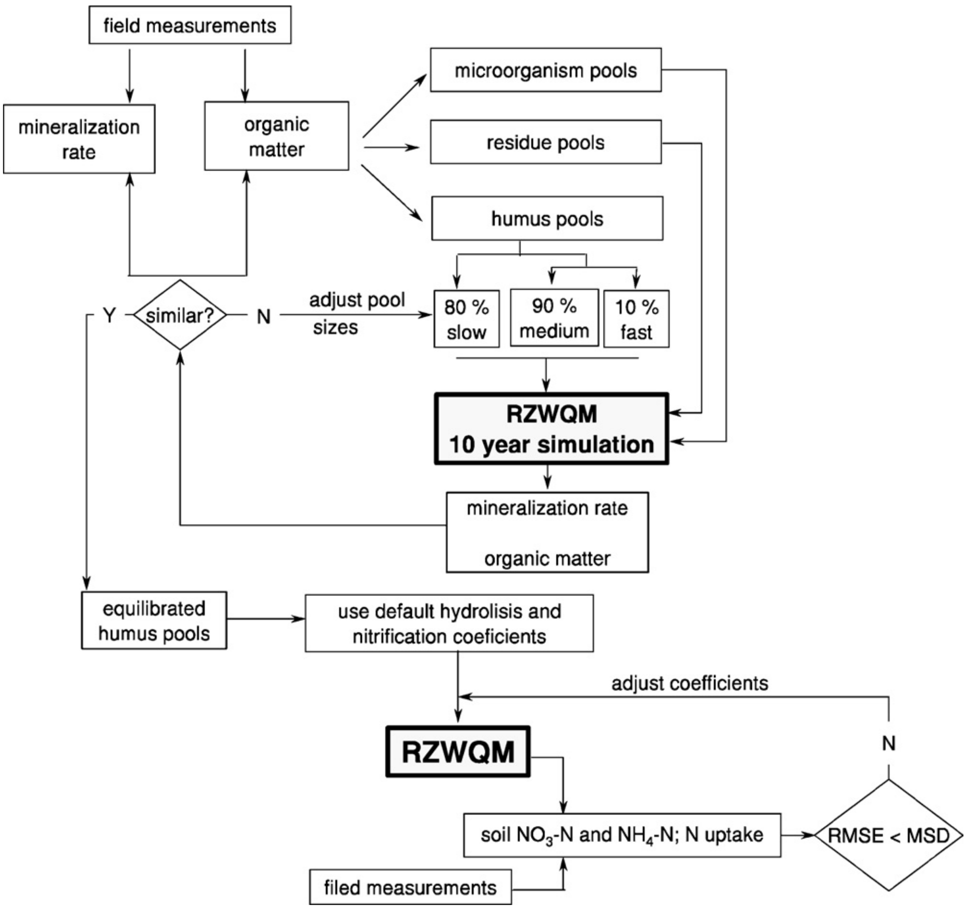

Fig. 5 – Flow chart describing the calibration of the nitrogen component of RZWQM.

magnitude as the observed, this step was completed. If not this step was repeated with a different initial partition of SOM among pools.

(iii) Calibrate the coefficients for nitrification and hydrolysis rates

These two coefficients (A_{nit} and A_u) are used to calculate the zero order nitrification rate $K0_{nit}$ (Eq. (2)) and the first order coefficient for urea hydrolysis, Ku (Eq. (4)). Calibration of these two processes is based upon the comparison of the simultaneous evolution in time and depth of the nitrate and ammonium concentrations after fertilizer application.

Model validation must be performed for distinct climatic and management conditions so the model can be tested for extreme boundary conditions. For this reason, the experimental measurement is generally less intense than for the calibration process. Thus, for this study the flux variables (e.g. nitrogen uptake rates and the leaching fluxes) were not measured or calculated from field data. Only state variables (crop yields, cumulative nitrogen uptake and soil nitrogen) were measured and used as control variables for the predictions. The model was validated using independent data collected during the 1998 crop seasons under the current management practices. The model outputs used for validation were crop N uptake, crop yield, NO_3-N storage by soil layer during the crop cycle, and NO_3-N residual storage at the end of the season.

Residual analysis of the predictions was based upon the coefficient of efficiency (EF) calculated as (Loague and Green, 1991; Legates and McCabe, 1999):

$$EF = \frac{\sum_{k=1}^{n}(O_k - \bar{O})^2 - \sum_{k=1}^{n}(P_k - O_k)^2}{\sum_{k=1}^{n}(O_k - \bar{O})^2} \qquad (13)$$

where P_k are the predicted values, O_k the observed values, n the number of samples and $\bar{O}$ is the mean of the observed data. The EF ranges from $-\infty$ (poor model), to one (perfect model). A value of zero for the EF indicates that the model is as good predictor as observed mean, while negative values indicate that the model is a worse predictor than the observed mean (Wilcox et al., 1990). Positive values for EF mean that the model is a better predictor than the observed mean and further evaluation should be performed using other indicators.

Legates and McCabe (1999) recommend the use of the RMSE (Eq. (11)) to quantify the errors in terms of the magnitude of the variable. The lower and expected value for the RMSE is zero. In the present work, the upper limit accepted for this statistic is the MSD (Eq. (12)). Loague and Green (1991) suggested the use of graphical displays in order to find trends, types of errors and distribution patterns.

4. Results and discussion

4.1. *Net mineralization rate*

The results of the net mineralization (mineralization–immobilization) experiment are presented in Fig. 6. Since no N fertilizer was applied to the soil, the only source for NH_4-N was the mineralization of the organic matter, and for NO_3-N was the nitrification of the NH_4-N. Because no plant N uptake or N leaching losses occurred, adding the storage variations for nitrate and ammonium, a net mineralization was calculated for each period between measurements. The average net mineralization rate was estimated as 0.5 ± 0.1 kg N ha^{-1} day^{-1} for the silty loam soil for the entire experimental period. This yields, for the nitrogen balance calculation period, a gain of 67 ± 13.4 kg N ha^{-1} of mineral N. The mineralization process in the sandy soil does not appear to be significant, which is in agreement with the slightly acid pH of this soil and its low organic matter content.

Although the conditions of the mineralization experiment were not the same as the ones in the irrigated crop fields, these experimental values can provide an approximate magnitude to expect for the simulated mineralization rates and are used to control the calibration of the pools composition.

4.2. *Calibration of the pools composition*

After equilibration (10 years simulation) of the SOM and MBM pools, the simulated SOM content was, for both soils, similar to the measurements (Table 4). The average mineralization rates simulated for the two crop growing seasons were in the same order of magnitude as the ones that resulted from the field experiments. So the calibrated humus and microorganism pools were accepted as the initial conditions for the simulation (Table 5).

4.3. *Calibration of the nitrification and hydrolysis rate coefficients*

The simulations performed with the default values for the nitrification (A_{nit}) and hydrolysis (A_u) coefficients showed that

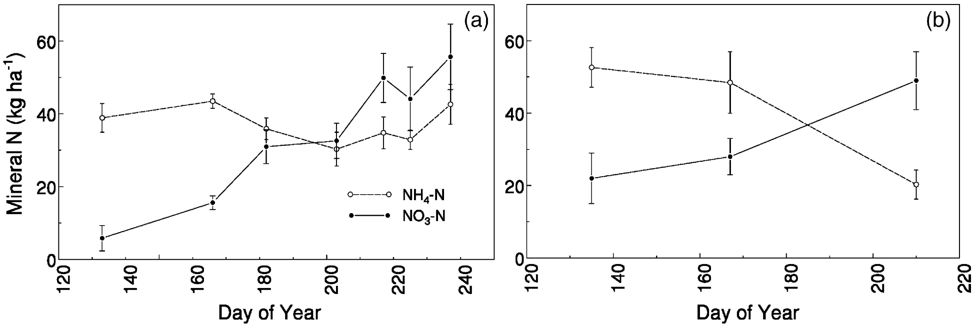

Fig. 6 – Results of the *in situ* net mineralization experiment (averages of nine replications): (a) silty loam soil; (b) sandy soil.

Table 4 – Results after OM pool equilibration (10 years simulation)

Soil type	Organic matter (%)		Mineralization rate (kg N ha^{-1} day^{-1})	
	Simulated	Measured	Simulated	Measured
Silty loam	1.32	1.26	0.37	0.5 ± 0.1
Sandy	0.85	0.92	0.05	0 ± 0.01

the model was not computing with accuracy the transformations of the different N forms in the fertilizer. Therefore, these coefficients were calibrated until the RMSE of simulations was lower than the MSD of the measurements for plant N uptake and soil nitrate-N (Table 6, Figs. 7 and 8). The lower nitrification rate coefficient for the silty loam soil in comparison with the sandy soil was justified by the 24–48 h saturation periods following the level basin (flood) irrigation, reducing the activity of the nitrifying organisms (Harmsen and Kolenbrander, 1965). The hydrolysis coefficients have the same order of magnitude for both systems.

Fig. 7a and b shows respectively the plant N uptake rate and the cumulative N uptake for grain corn in the silty loam soil. In both cases the RMSE of the simulations is lower than the MSD of the measured data. Fig. 7c shows the partitioning of N between the different plant parts although this was not considered initially as a control variable for the calibration. The same results are shown in Fig. 8 for the forage corn in the sandy soil. Again the RMSE is lower than the MSD. These good results of N uptake and partitioning in the plant are due to the good simulation of plant biomass and water uptake (Cameira et al., 2005) and also to the good simulation of the N transformations in the soils.

Fig. 9 shows the evolution of soil nitrate-N storage during the grain corn growing season. The large standard deviation of measurements shows the field variability associated with soil nitrate-N and difficulty in the evaluation of the model performance. These large standard deviations of measured NO_3-N concentrations were also found by several other researchers (Kengni et al., 1994; Netto et al., 1999; Schoen et al., 1999). The reasons include the spatial variability of the soil and the management practices influencing the processes associated with soil C/N dynamics.

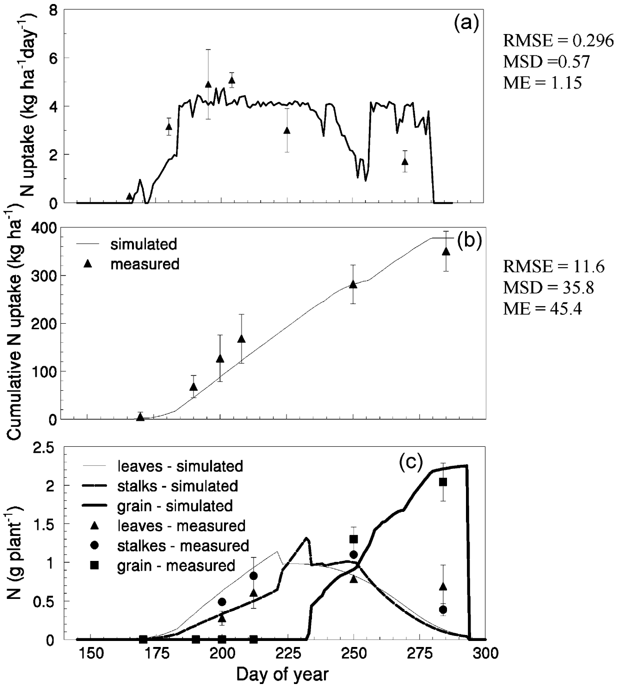

Fig. 7 – Nitrogen in the plant: (a) uptake rate; (b) cumulative uptake; (c) N partitioning between the plant parts. Silty loam soil, calibration phase (RMSE: root mean square error; MSD: mean standard deviation of measured data; ME: maximum error).

The fertilization treatment in this plot consisted of ammonium application on day 144 and UAN (50% urea + 25% ammonium + 25% nitrate) on days 183 and 255 in 1996. Since the RMSE is always lower than the MSD, we can conclude that the model simulates with the required accuracy the transformations between the different N forms, meaning that the hydrolysis and nitrification coefficients were successfully calibrated. The same for the sandy soil (Fig. 10) where the fertilization treatment consisted of urea + nitrate on day 146 and urea on day 202 in 1997.

Fig. 11 shows the drainage fluxes, calculated by Cameira et al. (2005) and the NO_3-N leaching in the sandy soil,

Table 5 – Distribution of OM between the humus pools after equilibration (10 years simulation)

	Silty loam soil		Sandy soil	
	Fast + medium (%total)	Medium (%fast + medium)	Fast + medium (%total)	Medium (%fast + medium)
Default	5	90	5	10
Equilibrated	6	50	10	18

Table 6 – Calibrated parameters for the nitrogen transformations

Process	Rate coefficient	Default values	Calibrated values	
			Silty loam soil	Sandy soil
Nitrification (Eq. (2))	A_{nit} (day^{-1} organism^{-1})	1E−9	2E−10	1E−8
Hydrolysis (Eq. (4))	A_u (day^{-1})	4.7E−4	1.5E−4	2.5E−4

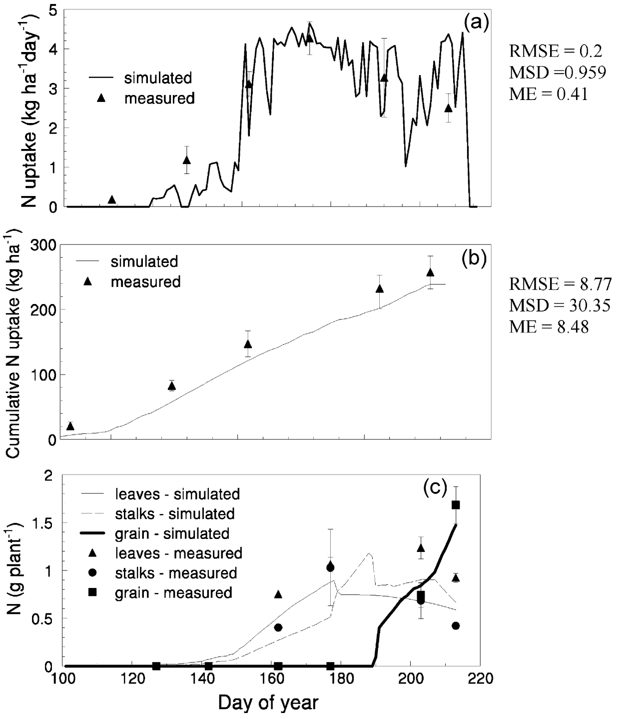

Fig. 8 – Nitrogen in the plant: (a) uptake rate; (b) cumulative uptake; (c) N partitioning between plant parts. Sandy soil, calibration phase (RMSE: root mean square error; MSD: mean standard deviation of measured data; ME:– maximum error).

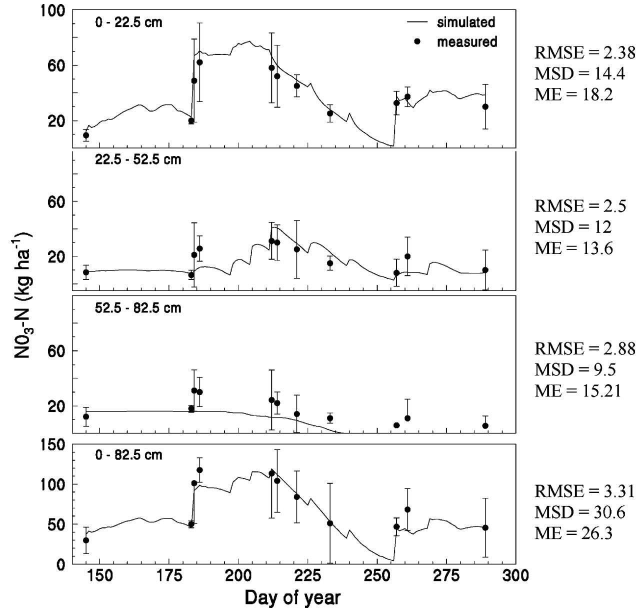

Fig. 9 – Measured and simulated NO$_3$-N storage in soil (averages of nine replications). Silty loam soil, calibration phase (RMSE: root mean square error; MSD: mean standard deviation of measured data; ME: maximum error).

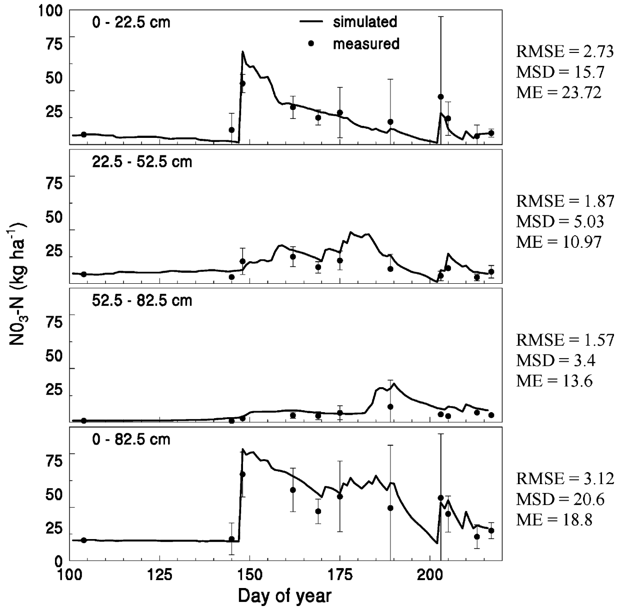

Fig. 10 – Measured and simulated NO$_3$-N storage in soil (averages of nine replications). Sandy soil, calibration phase (RMSE: root mean square error; MSD: mean standard deviation of measured data; ME: maximum error).

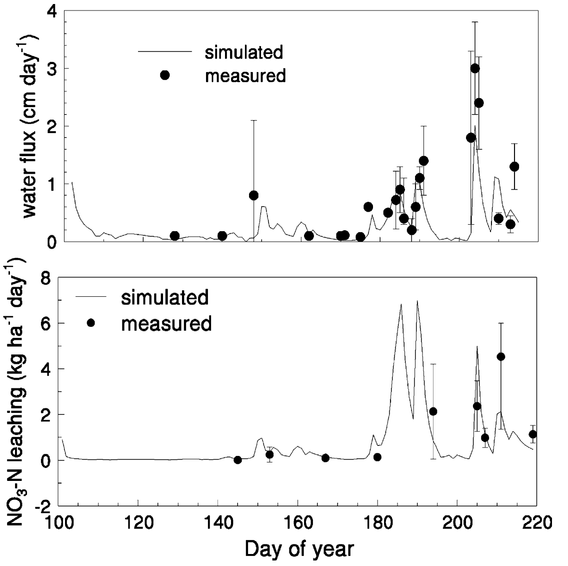

Fig. 11 – Simulated and measured drainage and leaching fluxes through the bottom of the root zone (82.5 cm). Sandy soil, calibration phase.

calculated by Eq. (9). The large standard deviations for both the drainage and leaching fluxes reflect the uncertainty associated with the use of the Darcy equation to compute water fluxes in this type of soil. Besides soil heterogeneity, this uncertainty is due to the high hydraulic conductivity of this soil for high moisture contents, which magnifies the error of the flux estimates when a small error occurs in the estimation of the hydraulic gradient. Nevertheless, in most of the cases there is an agreement between the observed and the simulated drainage occurrence and peak height. For the silty loam soil,

Table 7 – N related simulation errors after model calibration

N mineral (kg ha^{-1})	Measured	Simulated	Error (%)
Silty loam soil			
Net mineralization	67.6 ± 13.4	67.5	−0.14
Root uptake	325 ± 41.8	370.0	13.8
Residual storage	45 ± 36	47.0	4
Sandy soil			
Net mineralization	0 ± 1.2	2.0	
Root uptake	250 ± 3.7	240.5	−9.8
Residual storage	22.6 ± 6.1	25	10.6

no leaching was observed through the soil matrix due to a persistent capillary rise from the water table.

Table 7 shows N related simulation errors after calibration for both soils. Nitrogen root uptake was simulated for both soils with errors between 10 and 14%. The residual soil profile nitrate-N has low simulation errors, 4% for the silty loam soil and 10.6% for the sandy soil, which are within the range of measurements.

4.4. *Validation*

The model was validated for both cropping systems using independent data collected during the 1998 crop seasons. Fig. 12 shows the predicted NO_3-N storage by soil layer and for the entire profile for the silty loam soil. On day 159, 200 kg of urea were applied to the crop (Table 3). As the top graph shows, the model predicted with accuracy the hydrolysis and nitrification processes. We can conclude that the correspondent rate coefficients were successfully calibrated. Fig. 13 shows the predicted NO_3-N storage by soil layer, for the entire profile and for the three fertilizer treatments in the sandy soil. The graphs show that the model is predicting the trend of the measured data, reflecting the different N amounts applied in each treatment on day 146. Day of year 125 is an exception. In all of the treatments, 72 kg ha^{-1} of ammonium was applied to the crop on day 109 (Table 3). This amount does not explain the variation in storage of 145 kg ha^{-1} between days 125 and 109 for all the treatments. Furthermore, the simulations for the rest of the days are close to the observations. For these reasons it was decided not to include day 125 in the analysis of the residual errors.

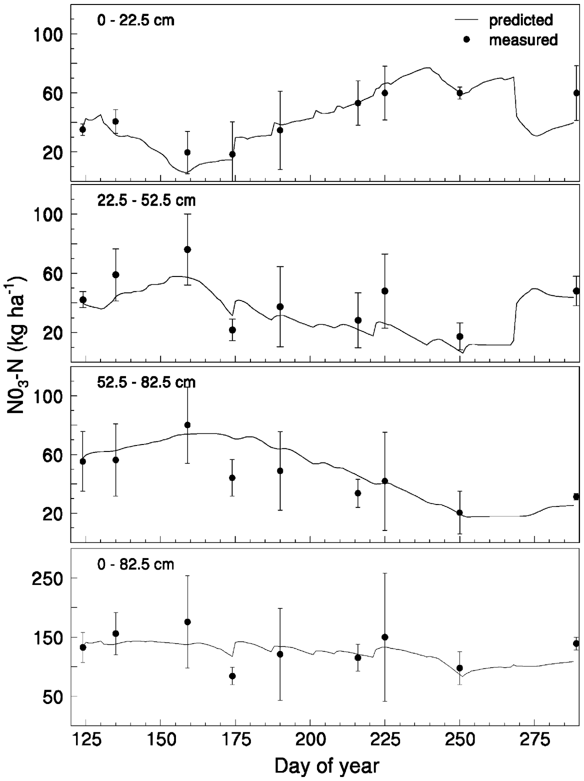

Fig. 12 – Predicted and measured NO_3-N storage by soil layer and for the entire profile (averages of nine replications). Silty loam soil, validation phase.

Fig. 14 shows the distribution of the NO_3-N storage in the soil during the crop cycle over the 1:1 line, reflecting that in spite of the deviations between measured and predicted values, the model predicted the response of NO_3-N storage in the soil profile to the different fertilization treatments.

Table 8 shows the residual errors for the NO_3-N storage predictions for the soil profile (0–82.5 cm) for both soils. EF is sometimes less that 0.5, but always positive, meaning that the model explains the variability of measured data, and that other indicators should be used. The interpretation of this statistic is difficult, being often and wrongly interpreted like the statistics R^2 (coefficient of determination), that is, a value of 0.5 is usually interpreted as a mediocre model. EF has a different meaning. Legates and McCabe (1999) illustrate that the EF is more sensitive to extreme values than to observations near the mean due to the squaring of the differences. Also, this statistics shows higher values when the observed means have a large temporal variability. For the silty loam soil the average soil nitrate-N is fairly constant with time (S.D. = 29 kg ha^{-1}), therefore, a low EF (0.34) is calculated even though the RMSE is much lower than the MSD. For the sandy soil, an EF value of 0.77 was calculated for treatment A, which has higher temporal variability in soil nitrate-N measurements (S.D. = 110 kg ha^{-1}). For treatments B and C the S.D. for the NO_3-N storage time series has values of 60 and 59 kg ha^{-1}, respectively, while the EF has a value of 0.45. For the tree treatments the RMSE is lower or very close to the MSD.

Since the measurements have a significant variability, the comparison between RMSE and MSD seems to be an adequate indicator for model performance. The RMSE values for model validation are larger than those of model calibration, but lower or very close to the MSD. For the silty loam soil RMSE of the NO_3-N storage is lower than the MSD. The same happens for the sandy soil, treatment B. Therefore, no simulation error can be quantified since the predictions are within the range of the measurement errors.

For the other situations RMSE is higher than the MSD, meaning that the predictions have an error. This error can be quantified by the indicator 1-RMSE/MSD. So, we can conclude that time series concerning NO_3-N storage in the soil profile were predicted with errors of 30 and 7%, respectively.

The number of trials presented in this study is not enough to make an overall classification of model performance. Nevertheless, the results indicate that the model is performing well since in three of the four cases the error was less than 7%.

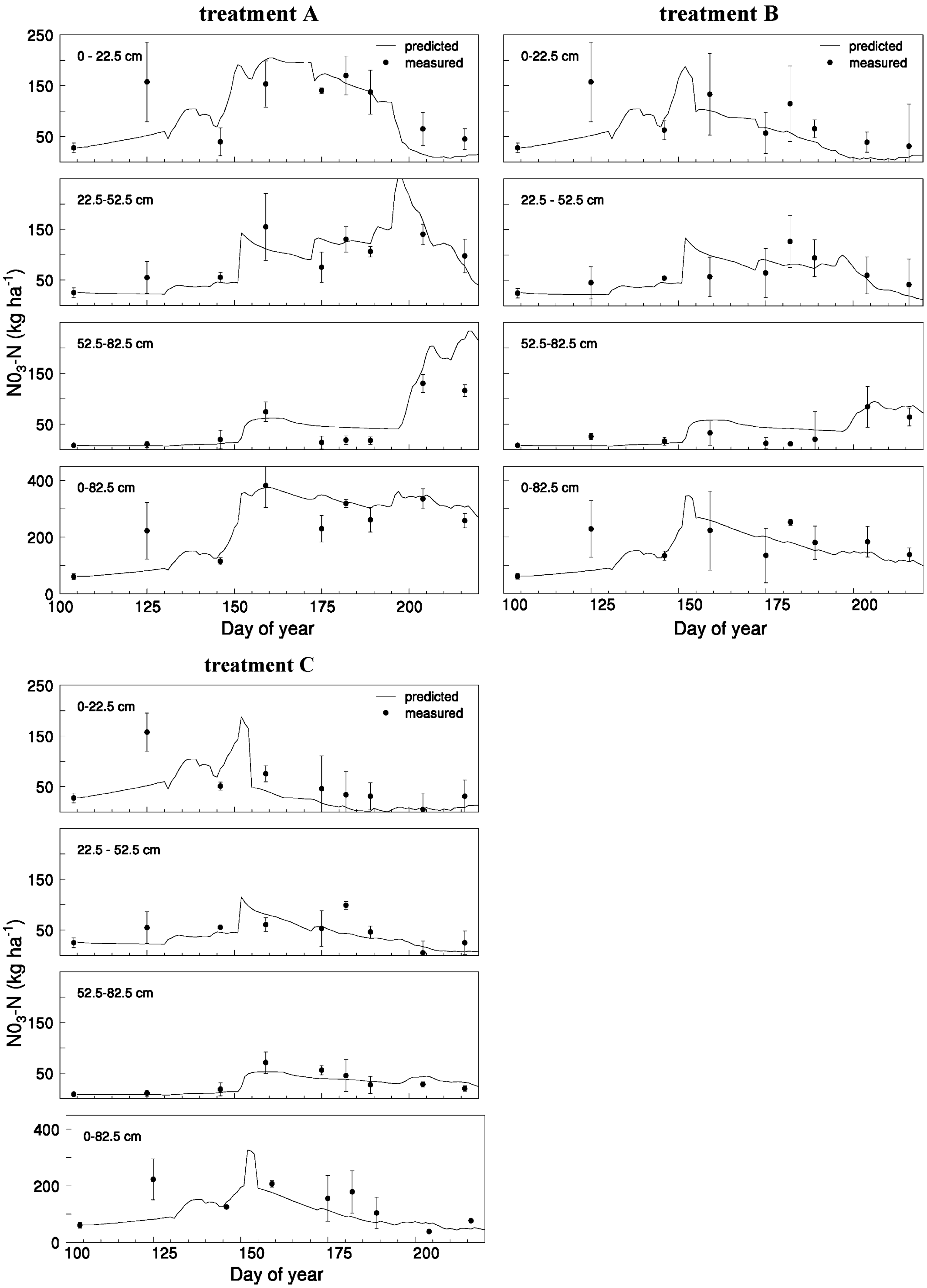

Fig. 13 – Predicted and measured NO_3-N storage by soil layer for the different fertilization treatments (averages of nine replications). Sandy soil, validation phase.

The worse results were obtained for the sandy soil and maybe related to the leaching of nitrate, which is not a significant process in the silty loam soil where no drainage fluxes occur. As shown in Table 9, crop yield was predicted with an error of 1.1% for the grain corn in the silty loam soil and with errors varying between 2.8 and −10% for the three fertilization treatments for the forage corn in the sandy soil. In all of the cases the predictions are in the range of the standard deviation of measurements. Nitrogen uptake was predicted with an error of 2.8% for the grain corn and with errors varying between −3 and −13% for forage corn. The highest prediction errors correspond to the residual soil NO_3-N profile, reflecting

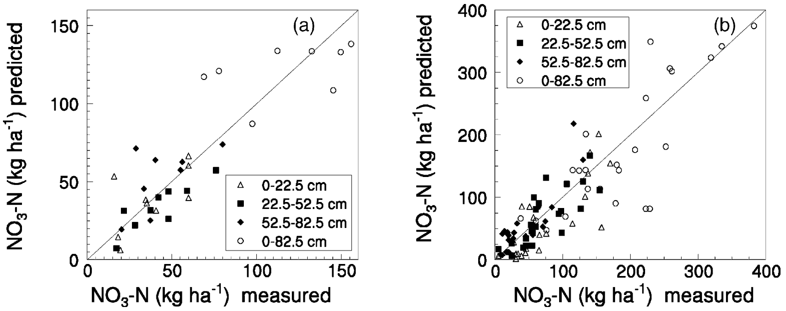

Fig. 14 – Predicted *vs.* measured NO_3-N storage by soil layer during the crop cycle (averages of nine replications) for: (a) silty loam soil; (b) sandy soil, all treatments (validation phase).

Table 8 – Residue analysis for the predictions of NO_3-N storage in the profile, for both soils

EF	RMSE (kg ha^{-1})	MSD (kg ha^{-1})
Silty loam soil		
0.34	22.1	44.7
Sandy soil		
Treatment A		
0.77	48.9	37.2
Treatment B		
0.45	41.7	66.0
Treatment C		
0.45	35.9	33.4

EF: coefficient of efficiency, RMSE: root mean square error, MSD: mean standard deviation of measured data.

the accumulation of the errors for the entire simulation period. For the silty loam soil the prediction error was −25% while for the sandy soil it varied between 19 and −38%.

The residual NO_3-N prediction errors are larger than the ones for the NO_3-N storage time series since the S.D. of the residual profile is smaller than the average S.D. of all the observations.

The potential BMP benefits to reducing residual NO_3-N cannot be distinguished better than the resolution of the model and its associated input data. For example, in this case the model showed a predictive resolution of 25% in the silty loam soil and ranging from 17 to 38% in the sandy soil for residual soil nitrate-N at the end of the growing season. These results indicated that, for the agricultural fields under study, the model was able to simulate climatic and management conditions different from the ones used for the calibration, since RMSE of the NO_3-N storage in the soil profile predictions was lower or very close to the MSD of the measured data. However, for the quantification of the uncertainty, validation must be performed for a wider range of conditions, including extreme climatic and management.

5. Conclusions

In this study, RZWQM was applied to two soil–crop systems representing different behaviors in respect to N transformations and movement in the soil profile, and different boundary

Table 9 – Prediction errors for N related variables (validation phase)

	Measured	Predicted	Error (%)
Silty loam soil			
Residual NO_3-N (kg ha^{-1})	145 ± 11.0	108.5	−25
N uptake (kg ha^{-1})	321 ± 5.6	330.91	2.8
Yield-grain (t ha^{-1})	11.2 ± 2.0	11.3	1.1
Sandy soil			
Treatment A			
Residual NO_3-N (kg ha^{-1})	258.4 ± 25	306.3	18.5
N uptake (kg ha^{-1})	283 ± 4.9	246	−13
Yield above ground, dry matter (t ha^{-1})	20.7 ± 3.3	18.6	−10.1
Treatment B			
Residual NO_3-N (kg ha^{-1})	137 ± 24	113.3	−17.3
N uptake (kg ha^{-1})	232 ± 3.2	225	−3
Yield above ground, dry matter (t ha^{-1})	17.8 ± 3.0	18.3	2.8
Treatment C			
Residual NO_3-N (kg ha^{-1})	76.1 ± 7.6	47.2	−37.9
N uptake (kg ha^{-1})	199 ± 1.5	190	−4.5
Yield above ground, dry matter (t ha^{-1})	16.9 ± 3.1	17.3	2.4

conditions (irrigation and fertilization amounts and timings). As it was shown in the previous paper (Cameira et al., 2005) and in the present work, each time RZWQM is used in a new soil–crop system, the model has to be calibrated. After calibration, the model was able to distinguish between two soils, and to predict different mineralization, nitrification and hydrolysis rates. The time series data for NO_3-N storage in the soil profile were predicted within the experimental errors for the silty loam soil and for one fertilizer treatment in the sandy soil. Prediction errors of 7 and 30% were obtained for the two other treatments in the sandy soil. Residual NO_3-N was predicted for the different systems with errors varying between 19 and −38%. Predictions for gain yield and forage yield were in the range of the standard deviation of measurements. N uptake was predicted with an error of 2.8% for the grain corn while for the forage corn the errors varied between −3 and −13%.

It was necessary to calibrate the different modules in order for the model to predict, with the required accuracy ($RMSE < MSD$) crop N uptake, crop yield and the N balance terms for the studied systems. The overall iterative methodology used for calibration was appropriate to better account for the strong interactions among plant development, root uptake for water and N and soil water and soil N storages. This work demonstrated an integration of field research with system modeling, and showed that, to obtain good N predictions (uptake, leaching and storage in the soil) and crop yields with the RZWQM:

(1) it was essential to first have a good estimation of the water balance components (evapotranspiration, leaching and soil water storage);
(2) it was necessary to start from the measured soil OM content and run a 10-year simulation to equilibrate the OM pool's composition;
(3) it was helpful to have field estimation of the net N mineralization rate in order to calibrate soil carbon/nitrogen processes;
(4) since the model is very sensitive to the nitrification and hydrolysis coefficients, it was suggested to calibrate these coefficients using simultaneous field measurements for soil nitrate-N and ammonium-N.

These results indicate that, for the agricultural systems under study, the model is able to simulate climatic and management conditions different from the ones used for the calibration with an accuracy that is acceptable in practical applications for complex and spatially variable field conditions. The next phase of the model application in these systems is to screen different management scenarios in order to select the agronomic practices that are more appropriate for these systems (BMP), considering the resolution shown by the model in the prediction of the different variables.

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