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Seasonal and land use impacts on the nitrate budget and export of a mesoscale catchment in Southern Portugal

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ABSTRACT

Stream nitrate nitrogen exports are an important indicator of agricultural impacts on aquatic health in catchments. Quantitative assessment of factors and processes affecting stream nitrate loadings is complex because of the large number of causal factors and processes, such as weather and rainfall, catchment hydrological behavior, soils, land use practices and biogeochemical processes. An eco-hydrological catchment modeling approach, using the SWAT model driven by detailed field data, was used to analyze the nitrate export and the components of the nitrogen budget of the 352 km^2 upper Roxo river catchment in Southern Portugal. A detailed eight-year record (2001–2008) of the monitoring of weather, reservoir inflow, stream biogeochemistry, soils, in-stream and groundwater quality, and fertilizer application was used to calibrate and validate the streamflow and nitrate loadings obtained by the model. Results indicated a strong seasonal variation in nitrate exports, closely related to temperature and rainfall. Monthly nitrate loadings varied from 0.02 to 2.48 $kg\,N\,ha^{-1}$ during summer and between 0.03 and 14 $kg\,N\,ha^{-1}$ during late autumn and winter. Stream nitrate values, ranging from 1.5 to 16.5 $mg\,N\,L^{-1}$, were strongly related to extreme rainfall occurrences and wet periods. Detailed analysis of nitrate budget components at the sub-catchment level enabled evaluation of the impacts of the various processes affecting the nitrate nitrogen pool of the catchment. Besides high fertilizer inputs for annual crops, it was shown that biological nitrogen fixation and wet deposition by rainfall should be accounted for in input balances. Where denitrification naturally reduces nitrate levels in soils, streams and the reservoir, the largest contribution to stream nitrate originates from leached soil nitrate reappearing in groundwater baseflow, compared with less than 2% from direct surface runoff during high rainfall events. A fertilizer reduction scenario was effectively implemented to evaluate remedial nitrate control policies in accordance with the European Nitrate and Water Framework Directives. Agricultural practices and seasonal weather fluctuations were the main reasons for temporal variations in nitrate export via small streams to the main reservoir.

1. Introduction

Nitrogen levels in streamflow are important indicators of environmental catchment conditions (Piatek et al., 2009; Mulholland et al., 2005; Arheimer and Brandt, 1998). A multitude of human activities, such as agricultural practices or urban residual waste water effluent releases, may produce an excess of nitrogen supply in a catchment, and can lead to increased nitrogen losses, especially in the form of nitrate nitrogen (nitrate), thus disturbing and impacting the water quality of ecosystems (Ventura et al., 2008). Concern about nitrate impacts on freshwater bodies from activities such as agriculture dates back more than 40 years ago, when the Commission of the European Community (CEC) became interested in maximizing the fertilizer potential of animal slurry applied to agricultural areas (Sluijsmans, 1978). Nowadays, it is still a concern in the European Water Framework Directive, whereby several agriculture-dominated regions across Europe have been classified in the European Nitrate Directive 91/676/CEE as areas vulnerable to nitrate contamination from agricultural sources.

The Roxo river is an upper tributary of the Sado basin and is located in the important agricultural Alentejo region of Southern Portugal. The catchment area is within the zone of influence of the large Alqueva dam and reservoir, and has been classified as a vulnerable zone since 2006 according to the European Nitrate Directive 91/676/CEE. The Roxo upper catchment (352 km^2) drains into a reservoir, which is the main source of the domestic water supply for Beja city, as well as the water supply for the local mining industry and some important irrigation areas (ABROXO, 2009). The reservoir has, however, been under considerable water stress for several years owing to the combination of interannual weather variability that affects natural rainfall supply, increased water consumption, and contamination threats of varying origin

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(UNEP, 1997). There is serious concern among the local and regional authorities regarding the Roxo reservoir, related to both water quantity and quality.

Several field studies and data from the Roxo catchment have indicated high nitrate concentrations, around 15 mg N L^{-1} in small streams and shallow groundwater (Vithanage, 2009; Gurung, 2005; Chisha, 2003). Gurung (2005) suggested that the Roxo reservoir is a hypertrophic system, because maximum nitrate concentrations of 14 mg N L^{-1} and high values for other eutrophication indicators such as phosphorus and chlorophyll-a were regularly observed in the reservoir. Vithanage (2009) recorded NO_3^- levels ranging from 2 to 13 mg N L^{-1} in streams located in the southern part of the catchment, which in fact significantly exceeds the nitrate levels (5.65 mg N L^{-1}) established by the European Water Framework Directive (2000/60/EC). However, it is known that only a small percentage of the net nitrogen pool in a catchment is generally exported to streams (Boyer et al., 2002), while the rest is retained or lost in the watershed system through denitrification or volatilization into the atmosphere before reaching the water body (Filoso et al., 2003). Nevertheless, nitrate export studies remain important because excess nitrogen inputs in a water body can dramatically increase primary productivity and decrease the water quality of the impoundment (Alvarez-Cobelas et al., 2008; Caraco and Cole, 2001). Observation of high nitrate concentrations in natural waters may also be indicative of the possible presence and flows of other nutrients (e.g. phosphorus) or contaminants (e.g. pesticides).

Several studies consider an observation period of five years or more as sufficient for nitrate export studies, since this enables the spatial and temporal variability involved in the seasonal periodicity of nitrogen fluxes to be captured (Alvarez-Cobelas et al., 2008). Local medium-term studies have proved to be better than single-year analyses when it comes to understanding the controlling factors of catchment nitrogen fluxes (Alvarez-Cobelas et al., 2008; Schilling and Zhang, 2004).

The nitrate export of a catchment is affected by environmental factors such as ambient temperature, rainfall, runoff, streamflow, soils and land use, including agricultural practices such as fertilizer application and potential point sources (Schilling and Zhang, 2004). Catchment studies carried out in Europe have reported nitrate export values ranging from 0.4 kg N ha^{-1} to 17 kg N ha^{-1} yr^{-1} (Alvarez-Cobelas et al., 2008; Isidoro et al., 2006). With regard to the Roxo catchment in particular, mineral fertilizer, manure and residual waste water disposal are potentially major non-point sources of excess nitrogen.

The aim of this study is to estimate the nitrate exports by streamflow from the small streams to a water reservoir in the Roxo catchment in Southern Portugal, in order to assess the relative importance of environmental factors such as rainfall distribution, streamflow, land use and agricultural practices affecting nitrate loadings and losses in a mesoscale catchment, and ultimately to predict the hydrological or biogeochemical processes controlling the stream nitrate dynamics. The Soil and Water Assessment Tool or SWAT 2005 eco-hydrological model (Neitsch et al., 2005, 2002) was used for this purpose, using an eight-year period (2001–2008) of monitoring data. The SWAT model has been extensively used to determine rainfall-runoff responses and nutrient loadings in streamflow and biogeochemical processes in moderately and poorly gauged catchments (Lam et al., 2009; Hu et al., 2007; Pohlert et al., 2005).

2. Materials and methods

2.1. Study area

The study area is located in the Roxo catchment in the Beja district of Alentejo province, Southern Portugal (37°46′44″N to 38°02′39″N latitude and 7°5′47″E to 8°12′24″E longitude; Fig. 1). With a catchment area of 352 km^2, it is considered a mesoscale catchment. The topography varies from nearly flat to gently sloping terrain, with elevations ranging from 123 m at the catchment reservoir outlet to 280 m.a.s.l. near Beja city.

Alentejo province alone yields 75% of Portugal's total wheat production (Paralta and Oliveira, 2005). The region and the Roxo catchment are dominated by agricultural activities. The major crops produced in the region are winter wheat, maize, alfalfa and sunflower as rotation crops, and olives, vineyards (grapes) and cork oak as perennial agricultural crops (Table 1). Agricultural land covers more than 80% of the catchment. Winter wheat and alfalfa, as intensive crops, commonly require around 100 kg N ha^{-1} yr^{-1} of fertilizer, whereas recommended nitrogen fertilization for maize is around 150–200 kg N ha^{-1} yr^{-1} (Paralta and Oliveira, 2005; personal communication M. Varela of Centro Operativo e de Tecnologia de Regadio (COTR) and R. Nobre of Escola Agraria do Beja, Portugal). For olive and oak plantations, fertilizer application and amounts are quite variable, and depend mainly on foliar analysis and tree age. However, an average application of 100 kg N ha^{-1} yr^{-1} is common practice for olive orchards in the production season (personal communication M. Varela of COTR). Fertilization of range and grassland is negligible and is an uncommon practice in Portugal. Some areas of natural forest and silvicultural activities are present in the south of the catchment. Literature related to fertilizer use in eucalyptus plantations indicates minimal use: about 60 kg N ha^{-1} applied at the start of the plantations (Filoso et al., 2003). Two other natural nitrogen input sources in the catchment are biological nitrogen fixation by crops such as alfalfa, and atmospheric wet deposition by rainfall.

Water in the catchment drains into an artificial impoundment, the Roxo reservoir (maximum volume approximately 10^8 m^3), which was built in the early sixties and is used for municipal water supply to Beja city and its approximately 161,000 inhabitants, for the local mining industry, and for irrigation water supply to several areas (ABROXO, 2009). The irrigation water volume accumulated in Roxo reservoir is not used within the catchment, but is used to irrigate areas downstream of the reservoir. Water for crop irrigation in the catchment area comes from shallow groundwater, which is pumped to center pivot systems to irrigate crops such as alfalfa and maize (Table 1). The sewage waters from Beja city are channeled to a waste water treatment plant, before the residual waters are released into the Chamine-Pisoes streams in the upper part of the catchment. This also yields an additional and relatively constant nitrogen input and loading in the upper catchment stream network. The reservoir lake and riparian area cover an average area of 11.9 and 20 km^2, respectively, and represent 3.38 4% and 10.2% of the total catchment area.

The long-term mean annual rainfall in the catchment region ranges from 500 to 550 mm. Soil survey using the FAO-UNESCO classification system identified four main soil types in the catchment: Luvisols, Litosols, Planosols and Vertisols (Sen and Gieske, 2005). The Luvisols cover 64% of the study area and are consequently the dominant soil type (Gamises, 2009). This soil type, with loam to clay loam texture, extends from the northeastern part to the southern part. Soil physical properties include texture, bulk density, available water capacity, saturated conductivity and organic carbon percentage (Table 2). We used measured soil properties at our own institution (Gamises, 2009; Gokmen, 2006) in combination with official Portuguese soil data and information (Cardoso, 1965).

2.2. Data collection and nitrate export prediction

For this study, water quality data and information on nitrogen were collected from various sources. Groundwater nitrate (Paralta

Table 1
Land use–land cover and crop management information in upper Roxo catchment.[a]

Land use–land cover	Crop information	Total area (km^2)	Total area (%)	Fertilizer use				Irrigation system		
				Crop stage	Fertilizer type or NPK	Amount (kg/ha)	Timing/dates	Irrigation type	Irrigation volumes (mm/period)[b]	Irrigation timing
Agricultural–arable land winter annual in rotation	Maize (irrigated)	8.84	2.52	Planting	15-35-00	100	June	Center Pivot	250–350	6–12 runs
				Boost	6-20-18	300	July			
				Mid/maturing	Nitro 32N	400	August			
	Alfalfa (irrigated)	4.95	1.41	Planting	20-20-00	200	June	Center Pivot	230–300	As above or variable
				Development	Nitro 27%	200	July–August			
	Winter wheat or barley, bare fallow	75.47	21.5	Planting	10-30-00	300	Begin November	No irrigation		
				Development 3 leaves stage	Nitro 27%	250	January–February			
Agricultural-mixed crops	Summer annuals pasture, long fallow	129.41	36.8	SWAT auto-fertilization option				No irrigation		
Agricultural-permanent crops	Olive groves	26.04	7.4	SWAT auto-fertilization option				Drip irrigation in new plantations (not included in SWAT)		
	Vineyards	6.28	1.8	–						
	Cork oak	25.70	7.3	–				No irrigation		
Water bodies	Ponds, reservoir	11.94	3.4	Not applicable	–	–	–	–	–	–
Semi-natural vegetation	Rangeland shrubs, etc.	28.51	8.1	Not applicable	–	–	–	–	–	–
Forest land	Eucalyptus, Pinus spp.	33.34	9.5	Auto-fertilization option				–	–	–
Urban fabric	Urban low density	0.34	0.10	Not applicable	–	–	–	–	–	–
Urban fabric	Urban high density	0.52	0.15	Not applicable	–	–	–	–	–	–

Crop and irrigated areas based on ASTER satellite image land cover classification (July 2004) and field survey. Irrigation volumes variable as a function of crop, soil type and period (spring, summer); from observed pivot data (Aman, 2004).

Table 2
Soil properties of upper Roxo catchment.

Soil type[a]	Sample depth (cm)	Clay (%)	Silt (%)	Sand (%)	BD ($g\,cm^{-3}$)	AWC (vol%)	K_{sat} ($mm\,h^{-1}$)	OC (%)
Cph	0–20	41.5	24.1	36.4	1.51	0.12	2.16	1.5
Bpc	0–20	41.9	23.6	29.8	1.87	0.12	0.78	0.9
Px	0–20	39.8	29.1	29.3	1.81	0.13	3.12	1.3
Vx	0–20	33.5	33.9	32.7	1.87	0.13	7.44	1.4
Sr	0–20	31.4	30.5	34.0	1.97	0.13	17.1	0.8
Vc	0–20	35.5	22.6	40.9	1.54	0.12	7.56	1.2
Ah	0–20	44.8	21.6	33.7	1.52	0.12	1.02	0.9
Ps	0–20	27.0	36.0	37	1.66	0.13	5.52	0.6
Sp	0–20	36.6	41.0	22.5	1.79	0.15	7.68	0.7
Pxd	0–20	21.8	32.4	43.6	1.59	0.13	11.8	0.7
Pb	0–20	37.4	31.4	30.2	1.55	0.12	4.08	0.8
Pag	0–20	25.3	34.8	39.9	1.69	0.12	5.88	0.8

BD, bulk density; AWC, available water capacity; K_{sat}, hydraulic conductivity; OC, organic carbon.

[a] Soil unit code from Cardoso (1965): Cph, Vertisol – calcareous black; strongly decarbonated Bpc, Vertisols – calcareous black, strongly decarbonated; Px, brown Mediterranean soils from non-cacareous rocks; Vx, red-yellow Mediterranean soils from non-calcareous; Sr, red-yellow Mediterranean soil from non-calcareous normal; Vc, red calcareous soils – red calcareous soils of semi arid climate; Ah, humic Vertisol; Ps, unsaturated hydromorphic soils – with eluvial horizon – Planosols; Sp, hydromorphic soils – hydromorphic organic soils; Pxd, brown Mediterranean soils from non-calcareous rocks – normals; Pb, hydromorphic soils – without alluvial horizon – not strongly unsaturated; Pag, hydromorphic-brown Mediterranean soils.

and Oliveira, 2005) and surface water hydrochemical and nutrient data were measured during several field campaigns between 2003 and 2009 (Vithanage, 2009; Gokmen, 2006; Gurung, 2005; Mekonnen, 2005; Chisha, 2003) and by the authors during the period 2008 and 2009. A comprehensive water quality monitoring dataset of the Roxo reservoir from the local water authorities (EMAS, 2008; SNIRH, 2008) was used for generating nitrate time series of the receiving Roxo reservoir water body.

Daily records of precipitation, air temperature, solar radiation, wind and relative humidity were obtained from automatic weather stations located near the Aljustrel and Beja areas, and were used to generate the SWAT weather inputs (data source ref. COTR). Long-term climate data were used to create the weather generator parameter files (Neitsch et al., 2005). Missing data for the model are automatically generated based on historical records (Hu et al., 2007).

Daily catchment streamflow, assumed as being equivalent to the total reservoir inflow, was generated using an inverted reservoir water balance approach. An extensive detailed daily dataset from 2001 to 2008 of precipitation, evaporation, reservoir storage volume, historical daily reservoir water levels and water abstraction data (water for irrigation, drinking and industrial purposes) was made available by the Portuguese authorities (ABROXO, 2009). A reservoir mass balance method was used to estimate the total catchment streamflow volumes in the reservoir. This technique consisted of estimating the reservoir inflow from the variation over time in the storage volume of the reservoir and the total of all outflows and losses from the reservoir (Vithanage, 2009). These inflow volumes were used to derive the streamflow into the reservoir.

Information on agricultural practices such as general land management, crop rotation, fertilizer use, type and times of fertilizer application, planting and irrigation were obtained from COTR and Escola Agraria Superior de Beja (Table 1).

In soils, nitrate is generally very reactive and can be added in different ways, either by rainfall, fertilizer or biological N fixation. Soil nitrate can be removed through various hydrological and biogeochemical processes, such as runoff, leaching, volatilization, denitrification or plant uptake (Neitsch et al., 2002). We estimated soil denitrification rates from laboratory experiments on the 12 soil units and land uses in the Roxo catchment. We followed an indirect approach of anaerobic incubation of soils adjusted with potassium nitrate (KNO_3) without the addition of organic carbon (Yeomans et al., 1992). Groundwater nitrate concentration and physical parameters were also measured during winter and

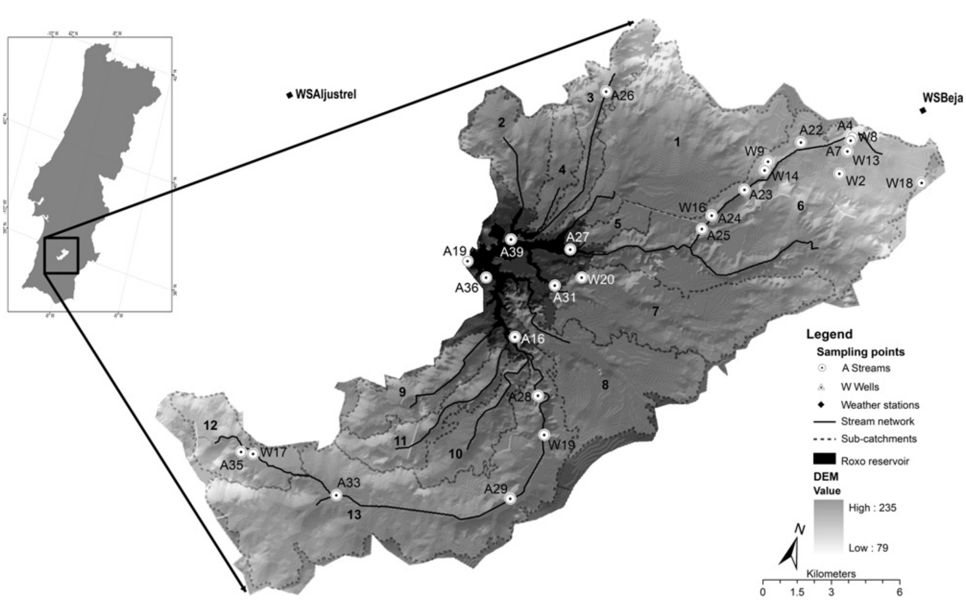

Fig. 1. Location of the study area.

summer 2008–2009, and obtained from literature for summer 2003 and 2005 (Paralta and Oliveira, 2005).

Streamflow, the catchment nitrogen budget and nitrate fluxes in runoff were estimated for eight years (2001–2008) using the SWAT 2005 model (Neitsch et al., 2005, 2002). The SWAT model was developed by the U.S, Department of Agriculture and the University of Texas (Arnold et al., 1998), and is a spatially distributed, physically based hydrological model that can operate on a daily, monthly, or annual time step. The data preprocessing is achieved in a two-step approach. First, the sub-catchments, streams, channel length and hill slopes are derived from a digital elevation model. Second, land use and soil classes are overlaid and multiple hydrological response units are generated within each sub-catchment. The climatic variables required by SWAT consist of daily precipitation, minimum and maximum air temperature, solar radiation, wind speed, and relative humidity. The model allows the input of observed daily records from weather stations or the generation of weather and climate variables using a built-in weather simulator. This generator uses long-term monthly means of the weather variables. The SWAT model includes large U.S. climate, soil and land cover–land use databases. To run the model in other regions of the world, it is necessary to create additional database records for weather, soils and land uses, using regional and local data. In this analysis, we generated all the parameters required to run the program as described by Bosch (2008), Chu et al. (2004), Hu et al. (2007) and Shanti et al. (2001). The catchment was divided into 13 sub-catchments based on a threshold flow accumulation area of 1000 ha. The combination of 10 different land uses, 12 soil units, and slope steepness resulted in the 243 hydrological response units used in the analysis.

Flow data from the period 2001–2004 were used for calibration, whereas data from 2005 to 2008 were used for validation using a monthly time step. Nitrate calibration and validation were carried out using datasets from 2003 to 2005 and from 2005 to 2008, respectively. The streamflow calibration process was completed by varying several SWAT hydrological parameters within their acceptable ranges (Table 3) in order to adjust the model-predicted monthly baseflow, streamflow and nitrate data. The SCS curve number (CN) method was selected to generate runoff volumes from rainfall. The CN values were initially parameterized using a combination of land use and soil properties. We used the standard procedures (USDA Natural Resources Conservation Service, 1986) to determine soil hydrological group and CN values. The percolation component used a storage routing technique to predict flow through each soil layer in the root zone. Lateral subsurface flow in the soil profile is calculated simultaneously with percolation. Groundwater flow contribution to total streamflow is simulated by routing a shallow aquifer storage component to the stream (Arnold et al., 2000). We verified baseflow using other refereed data and several field observations and measurements (reservoir inflows) made during the 2001–2008 simulation period by various authors (Mekonnen, 2005; Paralta, 2001). We added one complete parameter dataset for olive orchards to the crop inputs. This crop type was not included in the standard SWAT 2005 land use database. The insertion of this land use was performed by R. Srinivasan's SWAT development group at the Spatial Sciences Laboratory of Texas A&M University, College Station TX, USA (personal communication). Automatic calibration was selected mainly because manual calibration of the SWAT model for mesoscale catchments is not only tedious and time consuming but could also potentially lose final global outputs (Hu et al., 2007). After each simulation, SWAT outputs were evaluated for goodness-of-fit using three model performance indicators: the Nash–Sutcliffe coefficient (ξ_{NS}), the coefficient of determination (r^2), and the deviation of data being evaluated, expressed as a percentage bias or PBIAS (Moriasi et al., 2007).

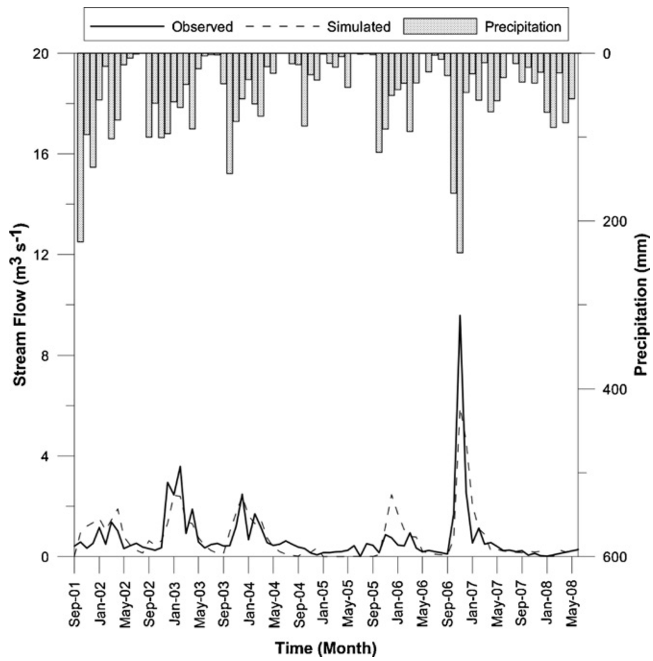

Fig. 2. Observed versus simulated monthly streamflow in the Roxo catchment and monthly precipitation for the eight-year record spanning the calibration period (2001–2004) and the validation period (2005–2008).

With regard to the nitrogen export data analysis, monthly nitrate loads were calculated based on total monthly streamflows multiplied by monthly nitrate concentration. Nitrate exports per unit area for each sub-catchment were estimated by evaluating the inputs versus outputs using the nitrate budget. Three agricultural management scenarios were included. A first scenario evaluated the water and nitrogen budget, based on standard practices but without irrigation in the catchment. In a second scenario, we evaluated the effect of the within-basin pivot irrigation practices on the water and nitrate nitrogen budget of the catchment. A third fertilizer reduction scenario was also implemented. In this scenario, the original values for nitrogen fertilizer application were reduced by 20% for maize, winter wheat and alfalfa, to explore the impact of fertilizer level on the nitrate budget and the water quality in the catchment and reservoir. Nitrogen data for precipitation were derived from EUSAAR (European Supersites for Atmospheric Aerosol Research).

3. Results

Daily and monthly streamflow of the Roxo catchment was successfully simulated, calibrated and validated by the SWAT 2005 model (Fig. 2). Monthly streamflow simulations were acceptable according to the statistical model performance measurements. Model prediction for calibration presented a Nash–Sutcliffe coefficient (ξ_{NS}) and the coefficient of determination (r^2) of 0.65 and 0.60, respectively (Table 4). The simulation showed that the model was acceptable for streamflow at the end of the summer (September–October). Mean monthly streamflow during the full analysis period (calibration and validation) averaged $0.83 \pm 1.56\, m^3 s^{-1}$, with the lowest monthly streamflow of $0.069\, m^3 s^{-1}$ occurring in July 2005, and the highest monthly streamflow of $9.54\, m^3 s^{-1}$ observed in November 2006 for the validation period. During autumn and winter months (e.g. November), high flows regularly occur after larger precipitation events (Fig. 2). In May, after the wet season, crop irrigation starts and stream discharge adopts a baseflow recession regime of around $1.09 \pm 0.73\, m^3 s^{-1}$ on average. Total average annual catchment

Table 3
SWAT model parameter calibration and sensitivity (upper Roxo catchment).

Parameter description	SWAT code	Parameter[a] sensitivity	Initial value	Adjusted value[b]
SCS runoff curve number (–)	CN2	1.86	Variable by HRU	[63–85] range
Threshold depth outflow from shallow aquifer (mm)	GWQMN	0.77	0.1	10.0
Capillary rise shallow aquifer to root zone coefficient (–)	REVAPMM	0.66	0.01	0.20
Base flow recession alpha factor (day)	ALPHA_BF	0.21	0.05	0.12
Soil evaporation compensation factor (–)	ESCO	0.21	1.0	0.65
Soil available water capacity (mm H_2O)	SOL_AWC	0.10	Variable by soil	[0.11–0.16] range
Soil depth of layers (m)	SOL_Z	0.08	Variable by soil	[0.4–1.2] range
Soil saturated hydraulic conductivity (mm h^{-1})	SOL_K	0.07	Variable by soil	[1.05–11.7] range
Leaf area index for crop (m^2/m)	BLAI	0.03	Variable by HRU	[0.0–5.2] range
Surface runoff lag coefficient (day)	SURLAG	0.02	4	2
Deep aquifer percolation fraction (–)	RCHRG_DP	0.02	0.05	0.10
Delay time (day)	GW_DELAY	0.01	20	12
Plant water uptake compensation factor (–)	EPCO	0.01	1.0	0.75
Parameter settings by user or SWAT 2005 default values				
Shallow aquifer initial storage (mm H_2O)	SHALLST	n.a.	0.1	200.0
Deep aquifer initial storage (mm H_2O)	DEEPST	n.a.	1000.0	1000.0
Fertilizer application fraction in topsoil 10 mm (–)	AFRT_LY1	n.a.	0.2	0.2
Rainfall nitrate concentration (mg N L^{-1})	CNR	n.a.	0.5	0.48
Denitrification rate coefficient (fraction)	CDN	n.a.	0.1	0.20
Humus mineralization (N&P) rate coefficient (–)	CMN	n.a.	0.003	0.01

[a] Mean parameter sensitivity as obtained from SWAT model sensitivity analysis using the Latin hypercube method (Van Griensven et al., 2006).
[b] Adjusted parameter values, after calibration.

precipitation over the study period was 518 ± 48.9 mm. Significant rainfall periods were registered during 2001, 2003 and 2006, with the highest values in 2006 (Fig. 2). Annual precipitation for 2006 was 718 mm, with extreme rainfalls totaling 237 mm in November. Precipitation during spring and summer was close to zero.

After calibration, the model predicted that, from the mean annual rainfall over the catchment area of 517.6 mm, 237.7 mm were removed through evapotranspiration, 48.8 mm were converted to direct surface runoff, and 237.4 mm percolated to the groundwater aquifer. From this initial drainage to the shallow aquifer, 9.2 mm re-entered the soil through capillary rise, 11.9 mm recharged the deep aquifer, and 216.3 mm appeared as baseflow in the stream network. Simulated mean annual catchment water yield and Roxo reservoir inflow for the whole simulation period amounted to 265.1 mm (Table 5).

Using calibrated model parameter data, the SWAT model successfully predicted nitrate load in the Roxo catchment (Fig. 3). For the calibration, monthly nitrate values showed ξ_{NS} and r^2 values of 0.60 and 0.70 (Table 4). Nitrate load increased with increasing streamflow (Fig. 3). The seasonal variation in nitrate was well reproduced in the calibration period, except for some overestimation occurring mainly during December 2003, when precipitation was higher than in other months and reached 143 mm.

The nitrate loadings during the validation period showed patterns similar to those in the calibration period. During the wettest months in 2006, slight overpredictions were found. The exception was in November 2006, when very high precipitation totaling 237 mm was registered and the nitrate load was underestimated (Fig. 3). The driest months fitted well in terms of both the range and the dynamics of nitrate. The ξ_{NS} and r^2 values for monthly nitrate load were 0.65 and 0.76, respectively. Seasonal variations in nitrate concentrations in streams displayed a seasonal pattern over the studied period. The concentrations ranged from 1 to 16 mg N L^{-1} and averaged 6.9 ± 2.7 mg N L^{-1} in late spring and in summer, and the highest nitrate values ranged from 3.10 to 16.5 mg N L^{-1} and averaged 7.4 ± 3.2 mg N L^{-1} in winter from January to February (Fig. 4). The simulation of monthly nitrate concentrations by the SWAT model was, however, rather poor when compared with measured data (Fig. 4). Although the simulation of increasing and

Table 4
Values of test statistics for SWAT model calibration and validation for Roxo catchment: PBIAS, ENS and regression coefficient of determination (R^2) for monthly stream flow and nitrate load.

Monthly streamflow	Calibration (2001–2004)	Validation (2005–2008)
Simulated mean flow ($m^3\ s^{-1}$)	0.88 ± 0.71	0.62 ± 1.23
PBIAS (% bias)	48	49
ENS (ξ Nash-Sutcliffe)	0.65	0.60
R^2 (coefficient of determination)	0.60	0.77
Monthly nitrate load	**Calibration (2003–2005)**	**Validation (2005–2008)**
Simulated nitrate load	6.24 ± 7.15	5.55 ± 8.16
PBIAS (% bias)	48	60
ENS (ξ Nash–Sutcliffe)	0.60	0.65
R^2 (coefficient of determination)	0.70	0.76

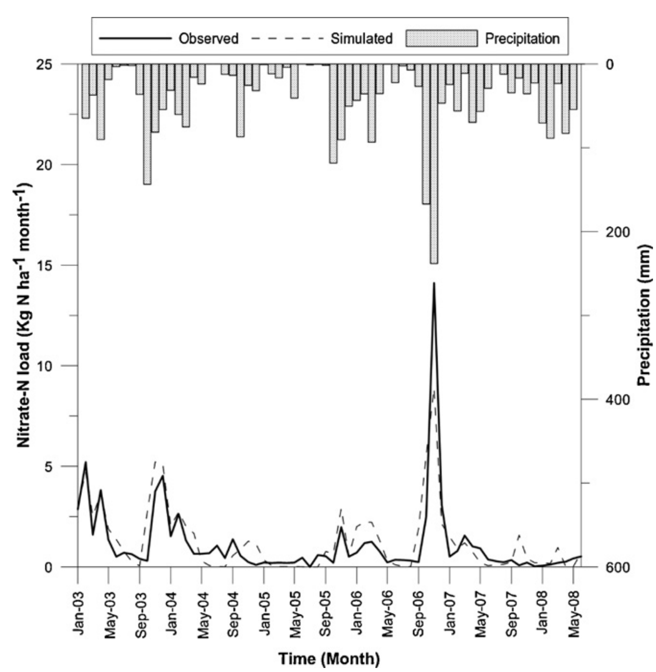

Fig. 3. Observed and simulated monthly nitrate loadings for the calibration period (2003–2005) and the validation period (2005–2008) and precipitation for the whole period.

Table 5
Annual water balance and nitrate budget components for agricultural management scenarios of the upper Roxo catchment.

Annual basin water balance (in mm H_2O)

	Precipitation (mm)	Surface runoff (mm)[a]	Total aquifer recharge (mm)[b]	Shallow aquifer capillary rise (mm)[c]	Deep aquifer recharge (mm)	Shallow aquifer baseflow (mm)[d]	Basin water yield (mm)	Evapo-transpiration or ETa (mm)	Potential or PET (mm)	Irrigation volume (mm)[h]	Soil water balance (mm)[g]
Scenario a: no irrigation from aquifer											
Mean[e]	517.6	48.8	237.4	9.2	11.9	216.3	265.1	237.7	1327.5	0.0	+2.9
Scenario b: center pivot irrigation from aquifer on summer crops (example case: maize and alfalfa on 3.8% of area – see also Table 1)											
Mean[e]	517.6	49.6	234.4	9.4	11.9	213.1	262.7	245.5	1327.5	11.2	–2.5

Annual basin area-averaged nitrate budget (in kg NO_3–N ha^{-1} yr^{-1})

	NO_3 input by fertilizer	NO_3 input rainfall	NO_3 in by biological fixation	NO_3 to shallow aquifer	NO_3 to deep aquifer	NO_3 in aquifer baseflow	NO_3 in Surface runoff	NO_3 loss denitrification	NO_3 uptake by plants	NO_3 export by crop harvest	Soil NO_3 balance[g]
Scenario a: no irrigation (from aquifer)											
Mean[e]	75.4	2.6	1.4	54.9	7.4	47.5	0.3	7.1	43.3	8.9	+8.2
Scenario b: center pivot irrigation from aquifer on summer crops (example case: maize and alfalfa on 3.8% of area – see also Table 1)											
Mean[e]	80.2	2.6	1.4	55.4	7.5	47.7	0.3	7.2	45.6	9.1	+12.2
Scenario c: 20% fertilizer reduction scenario (other conditions as standard practice scenario b)											
Mean[e]	64.1	2.6	1.4	50.7	7.1	43.6	0.2	6.9	41.3	8.5	+1.8

[a] Direct surface and lateral through the soil runoff.
[b] Soil percolation or aquifer recharge.
[c] Shallow aquifer capillary rise to root zone, incl. plant water re-use.
[d] Shallow aquifer outflow or base flow.
[e] 7-Year average over 30/09/2001–01/10/2008 period.
[g] Difference in soil water or nitrate storage between begin and end of simulation.
[h] Basin area-averaged irrigation volume from internal water source.

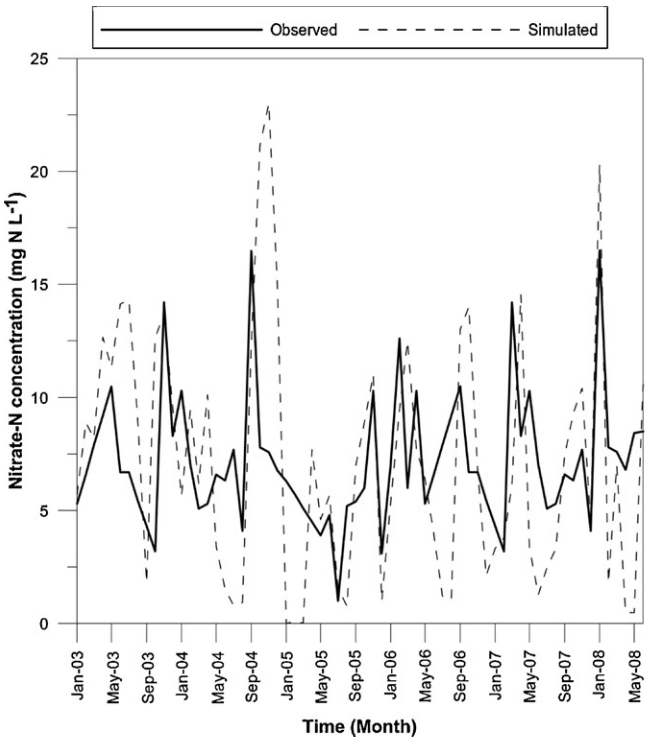

Fig. 4. Measured and simulated nitrate concentration values ($mg\,N\,L^{-1}$) in stream waters from 2003 to 2008.

peak nitrate concentrations was reasonably fair, the modeling of decreasing and low nitrate levels in streamflow seems prone to high uncertainty and errors. This can be partly explained by the relatively poor representation of riparian stream areas by the SWAT model.

The highest stream nitrate exports were observed for sub-catchments 1, 4, 9, 12 and 13 (Fig. 5), with winter wheat, maize, alfalfa and other intensive agricultural land use (i.e. sunflower and tomato) as prevailing crops. There was a significant positive correlation ($r = 0.5$, $n = 13$) between stream nitrate export by streamflow and total agricultural area in each sub-catchment ($p < 0.05$), as shown in Fig. 5. In this study, the SWAT model predicted inputs and outputs to evaluate the overall nitrate budget components. Major inputs were fertilizers and wet deposition by rainfall and biological N fixation (Table 5). The total basin-averaged inputs, which include fertilizers ($75\,kg\,N\,ha^{-1}\,yr^{-1}$), biological fixation ($1.4\,kg\,N\,ha^{-1}\,yr^{-1}$) and deposition ($2.6\,kg\,N\,ha^{-1}\,yr^{-1}$), reached $80\,kg\,N\,ha^{-1}\,yr^{-1}$ annually and thus are clearly dominated by agricultural practices in the catchment (Table 5). With regard to outputs, nitrate leaching was the most important output, representing $55\,kg\,N\,ha^{-1}\,yr^{-1}$ loading of the shallow aquifer (Table 5).

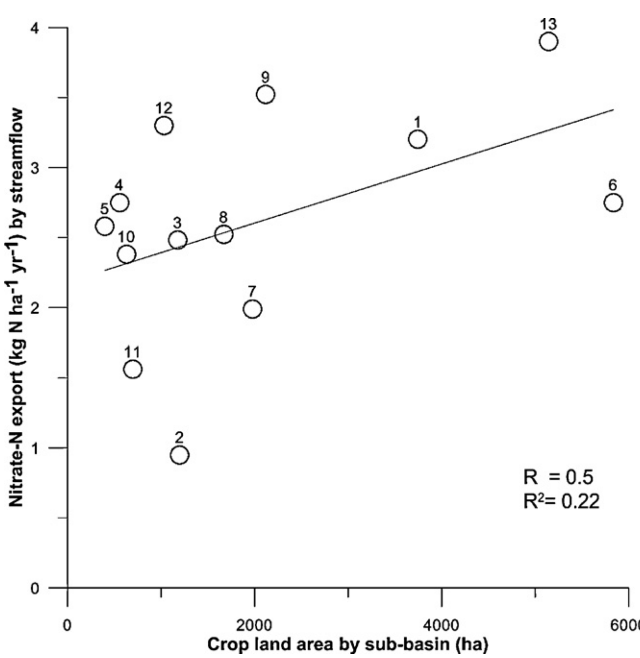

Fig. 5. Stream nitrate export by streamflow versus crop land area by sub-basin ($r = 0.5$, $p < 0.05$). Numbers in the figure correspond to the each sub-basin.

We also examined an irrigation scenario (Table 5) using shallow groundwater as water source, and considering a percentage irrigated area of 3.93% or 1380 ha of maize and alfalfa. The model predicted a slight increase in total catchment evapotranspiration of 7.8 mm (245.5 mm versus 237.7 mm). For the irrigated crop area itself, the increase in evapotranspiration amounted to 198 mm, from irrigation volumes of 286 mm received by the pivot systems (see also Table 1). Due to the limited irrigated area (3.93%), annual average catchment irrigation volume remains rather low at 11.2 mm. Basin water yield showed a slight decrease (262.7 mm versus 265.1 mm), owing to a lower shallow aquifer baseflow (Table 5).

The SWAT model predictions of the annual basin area-averaged nitrate budget (Table 5) indicated a slight increase in values for N fertilizer amount ($80.2\,kg\,N\,ha^{-1}\,yr^{-1}$), with no changes for wet deposition by rainfall ($2.6\,kg\,N\,ha^{-1}\,yr^{-1}$) and biological N fixation ($1.4\,kg\,N\,ha^{-1}\,yr^{-1}$). In terms of nitrate outputs, the annual basin area-averaged nitrate budget showed small increases in values for shallow aquifer leaching ($55.4\,kg\,N\,ha^{-1}\,yr^{-1}$) and uptake by plants ($45.6\,kg\,N\,ha^{-1}\,yr^{-1}$), when compared with the no-irrigation scenario.

4. Discussion

4.1. Streamflow prediction and nitrate load

The streamflow of the Roxo catchment was successfully estimated by the SWAT 2005 model for an eight-year simulation period (2001–2008). The model predictions generally performed well for a monthly time step during the calibration and validation periods and were concordant with guidelines established for monthly simulations (Moriasi et al., 2007). Coefficient of determination (r^2) and Nash–Sutcliffe simulation efficiency (ξ_{NS}) values (Table 4) supported the model predictions. We obtained a strong relationship between observed and predicted streamflow. However, slight over-predictions of streamflow at the end of the summers of 2001, 2003 and 2006 (September–October) were recorded. This is probably due to overemphasis on the direct runoff component versus delayed runoff (Bosch, 2008). Mean monthly streamflow showed a seasonal decreasing pattern, following a classic pattern for drier climatic areas (Molenat et al., 2007), with several smaller streams drying up during the summer (June–September). Components of the mean annual water balance (Table 5) showed that baseline hydrological calibration yielded mean annual values for direct surface runoff of 49 mm and baseflow of 216 mm. The baseflow fraction was found to be 81% of the total annual basin water yield of 265 mm.

In accordance with our study ($\xi_{NS} = 0.60$; $r^2 = 0.77$), similar nitrate studies using the SWAT model for small streams and reservoirs in the United States showed comparable efficiencies ($\xi_{NS} = 0.65$; $r^2 = 0.68$) for validation (Bosch, 2008). Chu et al. (2004) obtained ξ_{NS} values of 0.52 in a small agricultural catchment in Maryland, and Chaplot et al. (2004) predicted mean monthly nitrate loads in the Walnut Creek watershed ($51.3\,km^2$) in Iowa with a

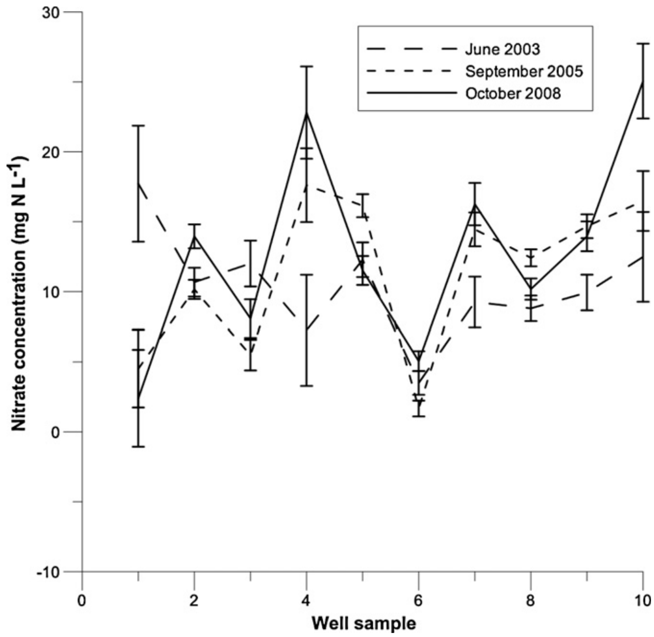

Fig. 6. Nitrate concentration in shallow groundwater (wells) during different sampling (June 2003, September 2005 and October 2008).

determination coefficient of 0.73. Nitrate load was overestimated strongly in November 2006 (a month with extreme excess rainfall), and this can be attributed mostly to the overestimation of streamflow. Moreover, when high rainfall occurs in the autumn and winter months, high nitrate levels in streamflow are noted, owing to important contributions from aquifer nitrate outflow. However, these NO_3^- concentrations in the baseflow stream may be overestimated, because the SWAT model does not account well for biogeochemical processes (e.g. denitrification) in the shallow aquifers, which naturally reduce nitrate levels in groundwater. It is also possible that the simulated nitrate load peak (9 kg N ha^{-1}) during the wettest months can be attributed to a simplification of shallow aquifer and baseflow processes such as nitrogen transformations and water flows. De Vos et al. (2000) found that higher nitrate values in the water table during winter were associated with the water flow and nitrate transport processes such as mineralization and denitrification. The highest nitrate loads (14 kg N ha^{-1}) were observed in the rainy season (November 2006), which can be attributed to the very high rainfall and runoff occurring during that month (Fig. 2). However, during the entire period relatively high nitrate concentrations reaching 16.5 mg N L^{-1} were recorded (Fig. 3). Therefore, water flowpaths, such as the soil to shallow groundwater to stream pathway, might play an important role in determining nitrate levels in catchment runoff. The SWAT model predicted that most of the nitrate loadings to the stream network would originate from baseflow, which was confirmed by the presence of a high nitrate concentration (11.6 ± 1.28 mg N L^{-1}) measured in wells during different samplings in 2003, 2005 and 2008 (Fig. 6) and other research (Paralta, 2001).

The nitrate loadings during the validation and calibration periods showed similar patterns. During the extremely wet month of November 2006, nitrate load was underestimated, whereas in the drier years (2004 and 2005) of the simulation period some slight overpredictions are visible (Fig. 3). Besides higher runoffs, the higher nitrate loads recorded in autumn can also be attributed to the increase in nitrogen mineralization during these months, which can be explained by warm ambient temperatures and relatively high soil moisture content. The drier months fitted well in terms of both the range and the dynamics of nitrate. The ξ_{NS} and r^2 values for monthly nitrate load were 0.65 and 0.76, respectively. Duarte et al. (2008) also used SWAT to simulate streamflow and nitrate loads in the Rio Formosa watershed located in the southern part of Portugal, using different periods for calibration and validation, and they obtained variations similar to those reported in this study. Nitrate export occurred mostly in rainy periods, and also with higher concentrations in baseflow. The high nitrate concentration in baseflow seems to be the result of increased drainage from a shallow fractured layer (Gabbros de Beja) present in the Pisoes sub-catchment area in the northern part of the catchment (Paralta, 2001).

Regarding the irrigation scenario for maize and alfalfa (3.93% of catchment area), the annual water balance components changed only slightly or remained the same (Table 5). This result is due to the relatively limited size of the total irrigation area, which is small in proportion to the total catchment area. The potential evapotranspiration, obtained using the PenMan–Monteith method, computed by SWAT and totaling 1328 mm for both irrigation and no-irrigation scenarios, is in agreement with previous recorded data and evaluations (1237–1376 mm) for the area (Paralta, 2001). A slight increase (7.2 mm) in actual evapotranspiration in the catchment water balance when irrigation is applied is rather obvious. The relatively low value is again due to the limited proportion of irrigated land in the catchment. Because irrigation and crop evapotranspiration are at the expense of shallow groundwater, a small decrease (−3.3 mm) in baseflow and basin water yield is noted, although the SWAT model predicted a slight (+0.8 mm) increase in direct surface runoff. Regarding the nitrate budget components, small increments in nitrate leaching and nitrate uptake by plants were found in the irrigation scenario (Table 5). The small difference in the components corresponds to the combined effects of fertilization and increased soil moisture content and water fluxes owing to irrigation.

4.2. Seasonal changes in nitrate export

The highest monthly nitrate losses were systematically recorded in autumn and winter, especially in November–December 2003 and December 2006 (Fig. 3). This can be explained mainly by nitrate accumulation in soils during drier periods (spring–summer), which is later mobilized and transported by higher rainfall, soil moisture, runoff and baseflow generation to the streams. Seasonal patterns of nitrate losses with significantly lower values during summer have been reported for agricultural catchments (Gao et al., 2004; Arheimer and Liden, 2000). One explanation for lower nitrate loss during this period might be the presence of stagnating waters in the catchment stream network during spring and summer periods, which in the case of high temperatures and low levels of oxygen are favorable for denitrification and act as nitrogen sinks in catchments. Another explanation is the increased plant uptake and removal by periphyton and plants (Flipo et al., 2007). Further, with the near absence of rainfall and very low streamflow in summer, much less nitrate is transported to the small streams in the catchment. Nearly 80% of the annual export of nitrate occurs from October to February. These results are comparable to those of an eight-year study by Beaudoin et al. (2005), which reported annual loads associated with amounts of drainage and flow in an agricultural catchment located in the north of France.

4.3. Land use and nitrate exports

In general, nitrate export is significantly related to the presence of local N sources, which vary according to land use distribution in the catchment. Sub-catchments dominated by agricultural fertilized crops such as maize, wheat and alfalfa exported five times more nitrate than sub-catchments covered by forest and range. In contrast, low nitrate export from forested sub-catchments is not surprising, because forests have high nitrogen retention capacity as they are subject to repeated biomass removal (Hayakawa et al., 2006). The agricultural sub-catchments (1, 4, 9, 12 and 13), where the highest export was registered (Fig. 5), have small ponds, mainly for irrigation purposes, which suggests that local aquatic environments also play a significant part in the processes controlling nitrate losses in the Roxo catchment. Monthly nitrate exports from agricultural catchments in Europe and the United States are similar to those found in our studied (Table 5) catchment (Isidoro et al., 2006; Beaudoin et al., 2005; Filoso et al., 2003; Bechmann et al., 1998; David et al., 1997).

4.4. Nitrate budget

The SWAT model offers the possibility of simulating the hydrological and chemical behavior of catchments and enables the overall nitrate budget to be quantified and evaluated. Only a few studies have conducted this analysis (i.e. Bosch, 2008; Hu et al., 2007). Our SWAT predictions enabled us to assess the biogeochemical transport in the Roxo catchment and to explain the causes and magnitude of nitrate fluxes. We identified the annual basin area-averaged nitrate budget and the main contributions of nitrate to the basin outflow (Table 5).

Major nitrate contributions to streamflow in the Roxo catchment originate from the use of fertilizer on maize, winter wheat, alfalfa and some minor crops. Corn or maize typically receives more fertilizer than other crops, around 150–200 kg N ha^{-1}. Symbiotic biological N fixation by Rhizobium bacteria can produce tens of kilograms of nitrogen per hectare per year, but is limited to only a few species of leguminous crops of economic importance (Olivares, 2008). Therefore, N fixation is considered an important input in agricultural fields where alfalfa is produced, and also contributes to nitrate exports to the streams and ultimately to the main reservoir. Basin-averaged N fixation (1.4 kg N ha^{-1} yr^{-1}) remains relatively low owing to the limited area of atmospheric N-fixing crops in the basin. However, high values have been found for alfalfa in studies in Alentejo, Portugal, where up to 100 kg N ha^{-1} yr^{-1} can be fixed (Ferreira et al., 2005). Our total N fixation value (1.4 kg N ha^{-1} yr^{-1}) is lower than the predicted inputs commonly found in semi-arid and agricultural fields such those found (4 kg N ha^{-1} yr^{-1}) in Southern Spain (González de Molina et al., 2010). Although our results showed that the main inputs for the whole catchment were fertilizers, biological fixation was more important in some sub-catchments (1, 2, 6 and 13), apparently being an important source of nitrogen in some of the catchment areas. The high nitrate inputs into the catchment have certainly influenced all components of the biogeochemical nitrogen cycle. These inputs commonly transform the ecosystem by high nitrogen export, increment of nitrate in groundwater, and increase of the denitrification process.

With regard to the outputs, most of the nitrate leaving the soil system is leached to the shallow aquifer and subsequently reappears as baseflow to the stream network and reservoir. According to the model, leaching to the shallow aquifer represented 75% of the soil nitrate losses in the catchment, amounting to 55 kg N ha^{-1} yr^{-1}. From this amount, 14% percolated to the deep aquifer and 86% or 47 kg N ha^{-1} yr^{-1} reappeared as baseflow nitrate in the catchment streamflow (Table 5). Results were compared and validated with nitrate concentrations (11.6 ± 1.28 mg N L^{-1}) from shallow groundwater from municipal and private wells, sampled during 2003, 2005 and 2008 (Fig. 6).

Plant nitrogen uptake is also important (43 kg N ha^{-1} yr^{-1}), but only a fraction of this (19%) is removed by crop harvest operations (Table 5). The basin-averaged nitrate removal by harvest operations was 8.9 kg N ha^{-1} yr^{-1}. In loamy soils in an agricultural field in the north of France, Beaudoin et al. (2005) found nitrate leaching values between 11 kg N ha^{-1} and 42 kg N ha^{-1}. This is in agreement with the values for most of the Luvisol and Vertisol soils in our catchment. It confirms that leaching is related to soil and crop types and farmer practices (Hall et al., 2001). In Luvisol in Elvas (South Portugal), Carranca et al. (1999) observed that an important part of N from fertilizer was lost by leaching, especially in autumn and winter. Hence, excess fertilizer application and nitrate leaching can be seen as the most important sources and pathway of increased nitrate loading in streams, with strong evidence of high nitrate leaching in the wettest periods (Boyer et al., 2006, 2002; Carranca et al., 1999). It would be beneficial to decrease the use of fertilizers during the autumn and winter periods in order to reduce nitrate leaching. Stream nitrate, however, was also strongly correlated with total runoff, reflecting the high mobility of this anion in general.

With regard to the denitrification processes, these were estimated to account for 11% of the total nitrate output of the catchment, with 7.1 kg N ha^{-1} yr^{-1} as basin area-weighted average. The highest values are found in sub-catchments 5 and 10, with 15.5 and 17 kg N ha^{-1} yr^{-1}, respectively, where several large ponds are present. These higher values correspond to denitrification rates found in hotspots in riparian areas surrounding water reservoirs in Eastern China (Wang et al., 2010, 2009). It is common to find that the small streams in the area are not active and are almost dry during spring and summer, with only the presence of local stagnant water spots. Certainly, these small ponds act as real riparian hotspots or buffers, with low oxygen values (<5.5 mg L^{-1}), temperatures reaching 35 °C in summer, high dissolved organic carbon values (>8 mg L^{-1}), high levels of sulfate (>125 mg L^{-1}) (unpublished data), and high levels of nitrate (16 mg N L^{-1}) in these stagnant waters in streambeds. If we combine these factors, we suspect that denitrification is a likely N output in the stream network. Limited literature indicates that denitrification in small seasonal and ephemeral streams is a seasonally important sink for nitrate before it reaches larger permanent streams and impoundments such as reservoirs and lakes. Lehmann et al. (2003) reported that during a stagnation period microbial nitrate reduction takes place in the stream water column when low oxygen conditions are present. Gentry et al. (2009) showed in-stream denitrification to be substantial during summer time.

The SWAT model losses by denitrification for the upper Roxo basin averaged 7.1 kg N ha^{-1} yr^{-1}. In our experimental measurements of potential denitrification in soils, we found the total mean denitrification rate in the Roxo catchment soils to be 3.9 ± 2.9 kg N ha^{-1} yr^{-1} (Gamises, 2009; unpublished data), which is to some extent in agreement with the model. Cheshire et al. (1999) reported that NO_3^- loss in soils around Beja city, inside the Roxo catchment, could be attributed to denitrification. In general, growing-season denitrification is not desirable on most agricultural and forested land because the denitrifiers are competing with plants for inorganic N. Molenat et al. (2007) pointed out that denitrification cannot be used to explain the NO_3^- decrease in a system when the conditions required for denitrification have neither been met nor become evident. We need a significant decrease in the soil or sediment redox potential and available organic carbon or pyrite, the most common electron donors for heterotrophic denitrification to take place.

Overall, our catchment nitrate budget component analysis indicates a slight positive N balance for the three scenarios (Table 5). This excess probably indicates over-fertilization, as the reduction scenario points to a lower N balance excess value. However, the uncertainties and simplifications in the biogeochemical processes simulated with the SWAT model do not permit us to draw more conclusions than an examination of the overall N balance.

In summary, our SWAT simulations enabled us to determine that excess fertilizer application is causing rapid (seasonal) nitrate leaching, probably by direct solute leaching (owing to limited microbial immobilization or lack of plant uptake) and increments in the mineralization in Roxo catchment. These processes can contribute to increasing soil acidity and diminishing soil fertility, as well as to impacts on water bodies through eutrophication, which nowadays is regularly observed and recorded in the main reservoir (EMAS, 2008; Gurung, 2005; Chisha, 2003).

4.5. Fertilizer scheme scenarios

During the last 40 years, the studied region has yielded 75% of the country's total wheat production (Paralta and Oliveira, 2005), but the amounts of fertilizer that are applied every year are not exactly known. Therefore, the cumulative chemical export to streams and reservoir impoundments so far is also unclear. Finally, there is little doubt that NO_3^- leaching and subsequent reappearance in the baseflow is a major source of nitrate in surface waters, contributing to local water quality problems and the nutrient loading of the Roxo reservoir.

A model-based analysis was carried out to assess best fertilizer management practices, with the intention of analyzing the impacts of a 20% reduction in current nitrogen fertilizer application rates. This percentage was in agreement with values used for the same agricultural crop conditions in similar catchments. The proportion chosen is also in accordance with European (EU) specifications within the framework of the Common Agricultural Policy (Council Regulation No. 2078/92/EEC), which advocates the adoption of environment-friendly farming practices. In order to protect water resources, farmers have to reduce the nitrogen fertilization level by 20% relative to the optimum level and establish catch crops before all spring crops. Furthermore, Bracmort (2010) suggested that a 20% reduction in nitrogen-based fertilizer from baseline applications of 10% and 20% is also useful in nitrous oxide (N_2O) mitigation alternatives for agricultural soil management.

Model outputs showed that a 20% fertilizer reduction can considerably decrease the NO_3^- exports (Table 5). Similar predictions for maize fields with a 20% fertilizer reduction have been reported for the United States by Jaynes et al. (2001), showing approximately 28% less NO_3^- export from maize fields. However, because most of the agricultural land in the Roxo catchment has been over-fertilized during the last 40 years, we cannot expect significant differences in the main crop yields and nitrate leaching in response to a reduction in fertilization. The soil nitrogen pools (organic and inorganic N) are high, and will change only gradually after a reduction in fertilizer N inputs in the soil system. It is also possible that the mineralization of the soil organic N was underestimated or the leaching or denitrification was overestimated, which reduced the nitrate before the plant uptake. Despite the fertilizer N rate reduction, the model predicted a small excess of nitrate, indicating some accumulation of N in the soil. One might expect that a fertilizer deficiency in crops would lead to a reduction in soil N (Jaynes et al., 2001).

5. Conclusions

This study of stream nitrate losses in the upper Roxo reservoir catchment was conducted using the SWAT model and eight years of observed weather, hydrological, chemical soil and water quality data. In periods with low leaching losses and minimal denitrification, nitrate is accumulated and carried over to the next year, thus partly offsetting the net depletion of soil N. Agricultural practices and seasonal fluctuations were the main reasons for high temporal variations in nitrate exports via small streams to the main reservoir. Our study suggests that seasonal fluctuations and winter wheat and maize agriculture play an important role in the variations in the nitrate losses via the stream network to the Roxo reservoir. In general, our catchment nitrate budget analysis indicates that N fertilizers are the largest inputs, but biological fixation and wet deposition by rainfall can also be important N sources and contribute to the catchment nitrogen budget. Nitrate export from the agricultural lands occurred mainly through soil leaching to the shallow aquifer and resulting baseflow pathway. The results of this study help us to quantify and understand the seasonal and land use impacts on nitrate loading patterns in the catchment. In the Roxo catchment, N fertilizer reduction schemes can be evaluated as possible control strategies, in terms of adjustment to the requirements of the European Nitrate and Water Framework Directives.

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