



Modelling Nitrate Reduction Strategies from Diffuse Sources in the Po River Basin

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Abstract: Water contamination caused by the presence of excessive amounts of nitrate can be catastrophic for aquatic ecosystems and human health. Due to these high risks, a great deal of emphasis has been placed on finding effective measures to reduce nitrate concentrations in rivers and aquifers. In this study, we used the SWAT model based on grid-cells of 5 minutes of resolution for assessing the processes involved in nitrate loads generation and transport into aquifers and rivers and for providing basin management strategies of nitrate reduction. We applied the model in the Po River Basin (Italy), one of the most densely populated and highly agriculturally exploited area in the Mediterranean basin. The model was successfully calibrated and validated in eight monitoring stations along the Po River for the period 2000–2012. Simulated monthly streamflow and nitrate concentrations were in good agreement with observations, obtaining values of bias around $\pm 25\%$ in both calibration and validation. Among the tested scenarios of nitrogen reduction from agricultural sources, red clover cover crop after corn, coupled with a targeted reduction of mineral fertilizers and the limitation of nitrogen manure leads to a reduction of nitrate leaching and nitrogen emissions of around 37%.

Keywords: diffuse sources; SWAT; Po River Basin; nitrate reduction; scenario analysis; agriculture management practices

1. Introduction

High nutrient concentrations in surface water and groundwater are still a major cause of water quality degradation. One of the main negative consequences of such degradation is eutrophication of water resources still pervasive in many lakes, coastal areas and rivers of the world due to diffuse nitrogen and phosphorus emissions that are the main drivers of this phenomenon [1].

In regions with intensive agriculture, surface water and groundwater are usually affected by anthropogenic pollution resulting from the use of high doses of fertilizers and inefficient irrigation techniques [2]. Indeed, fertilization input is recognized as the main diffuse source of nitrate contamination of water in agricultural areas [3].

The application of large amounts of mineral and organic fertilizers can contribute to excessive nutrient losses in rivers and groundwater. These losses can occur via surface runoff, sub-surface flow and leaching into aquifers. As a consequence, EU legislation, such as the Nitrates Directive [4] and the Water Framework Directive (WFD) [5], have enforced the limitation of nutrient losses to freshwater bodies through more careful management of agricultural land [6]. In particular, the Nitrates Directive requires the designation of nitrate vulnerable zones (NVZs)—areas which are polluted or at risk of being polluted by nitrates from agricultural nitrate pollution, where Codes of Good Agricultural

Practice must be put in place to reduce or control nitrate losses. Quantifying the effectiveness of these practices is key to the successful implementation of the directive. Indeed, the directive requires competent authorities to report monitoring data to assess its state of implementation. However, short-term monitoring data cannot completely capture the efficiency of measures put in place because of the lag time characterizing nutrient processes [7]. In this context, mathematical models can overcome this limitation allowing to identify and evaluate effective management strategies.

Modelling is considered extremely valuable as it can help quantifying the pollution and identifying its sources, and guiding decisions to improve management [8,9]. In particular, models were used in the initial stages of the WFD implementation to perform analysis of pressures and impacts, as well as during the design, setting up and surveillance of the monitoring networks and for the development of River Basin Management Plans [7].

There is a wide range of models with a large diversity of complexity and capabilities for simulating the impact of nitrogen mitigation measures, ranging from empirical methodologies (e.g., EXPORT coefficient [10]), conceptual models (e.g., GREEN-Rgrid [11]), to physical-based models (e.g., Soil and Water Assessment Tool, SWAT [12]). Their capabilities depend on the purpose for which they were developed. Their complexity and data requirements increase with the number of processes that they represent [7].

Scenarios of nutrient reduction discharge in the Mediterranean Sea are available [11], however they focus mostly on nutrient reduction at the source, assuming no impact on crop production and without considering the lag time in terms of response to a change in management. Consequently, in order to evaluate realistically the efficacy of measures in river basins, more detailed process-based models able to simulate in integrated way the impacts of agricultural management on water quality must be used.

The Soil and Water Assessment Tool (SWAT) [12] is one of the most used models for long-term simulation in predominately agricultural watersheds because it integrates the soil water and nutrient processes consistently, together with their impacts on crop growth and catchment hydrology [9,13–15].

In the Mediterranean area, the Po River Basin (Italy) is particularly problematic, with its surface aquifers containing generally high levels of nitrates, particularly in the lower Piedmontese plain (near the source of the Po River), in the Milan valley (central area of the Basin) and in the Emilia–Romagna plain (southeast area of the Po River Basin) [16]. About 22% of the basin was identified as NVZ, 80% of water withdrawal for civil and industrial comes from aquifers [17], and nitrogen leaching is the main problem affecting the quality of groundwater [18].

In the basin, approximately 70% of nitrogen (N) loads come from diffuse sources while 30% from point sources [19], and annual total nitrogen and nitrate (N-NO₃) loads transported to the Adriatic Sea in the period 2003–2007 were estimated at 166,552 ton/y and 86,295 ton/y, respectively [11]. Therefore, the reduction of nitrate concentration in aquifers and rivers of the Po Basin should focus on reducing diffuse nitrate losses from agriculture, by looking at alternative management options including mineral fertilizers strategies, manure management, and cover crops as conservation practice.

To test these hypotheses, we applied the SWAT model in the Po River Basin using a grid-cell approach employing the most recent global readily available datasets, with the following main objectives: i) calibrate and validate monthly streamflow, nitrate concentrations and loads in surface water in the Po River Basin, ii) provide long term mean annual water and nutrients balances for identifying the main pathways of nitrate pollution, iii) identify hot spots of nitrate contamination in rivers and aquifers that breach European drinking-water standards, iv) evaluate the effectiveness of diverse agricultural management strategies in reducing nitrate leaching and nitrogen emissions.

We start with briefly describing the Po River Basin, and then we give details about the model set-up, calibration and validation. Next, we present seven scenarios of nitrogen reduction from agricultural sources, and finally we discuss the results including the best alternative management practices to reduce nitrate leaching and identifying hot spots of nitrate concentration along the Po River where management efforts should focus.

2. Materials and Methods

2.1. Study Area: The Po River Basin

The Po River Basin is the largest Italian river system, with an area of about 74,500 km², a stream length of 652 km, 141 tributaries, 450 lakes and a delta area of 380 km² [20]. The basin covers seven Italian regions, and includes part of the Canton Ticino in Switzerland (Figure 1). Climate is influenced by the orography: it is typically alpine in the mountain zone, continental-warm in the flat basin area and Mediterranean on the coast. The average annual temperature is around 14 °C, ranging between 3 °C in winter and 25 °C in summer. The average annual precipitation is about 980 mm/y and the average discharge at Pontelagoscuro near Ferrara (Figure 1a) is around 1500 m³/s (period 1986–2001). The basin can be divided into three geographical regions: the Alps, the Apennines and the Po valley, where most of the economic and agricultural activities take place [19]. Approximately 33% of the studied area is agricultural (crops and fodder), 34% is forest and 25% is managed grassland (Table 1). The main crops are rainfed and irrigated corn, followed by rainfed wheat and irrigated rice. About 6% of the basin is irrigated (Table 1).

Land Use	Area (km ²)	Percentage (%)
Bare	804	1%
Fodder crops	12,848	17%
Forest	25,133	34%
Irrigated crops	4337	6%
Managed grassland	18,943	25%
Rainfed crops	7707	10%
Shrub	350	0%
Urban area	3297	4%
Water	1171	2%
Total	74,590	100%

Table 1. Land cover classes distribution in the Po River Basin.

Water withdrawal for civil and industrial use is about 5 km³/y, 80% of which is withdrawn from aquifer, while annual water use for irrigation is about 17 km³, of which 91% is abstracted from surface water [17].



Figure 1. Map of the Po River Basin with the main hydrographic network, regions border and monitoring stations used in this study (**a**). SWAT model discretization of the Po River Basin (**b**).

2.2. Model Description and Baseline Set-up

The Soil and Water Assessment Tool (SWAT; [12]) model is a process-based, semi-distributed model. It is widely used in large river basins to simulate water quantity and quality [21–23]. The model was selected because it has a flexible structure allowing to address different water resources and pollution problems, and it is well documented and open source. In this study, SWAT version 2012.664 was used

to simulate water quantity and quality in the Po River Basin and to assess the effectiveness of several selected strategies for the mitigation of nitrate emissions to aquifers and rivers.

The model operates at daily time steps and its major components include hydrology, plant growth, nutrient cycles, and land management [14,24]. In SWAT, a watershed is divided into subbasins, which are further subdivided into hydrologic response units (HRUs) that consist of unique combinations of soil, land use, and slope. The model structure comprises two phases: a land phase solved at HRU level, and a stream phase solved at reach level [25]. In the land phase, the HRU water, sediment and nutrients cycles in soil, and losses are simulated and then aggregated at the subbasin level. The movement of water, sediments, and nutrients through the stream are simulated in the routing (stream) phase.

SWAT requires input data related to topography, land use, soil, climate and land management. In this study, the inputs were kept consistent with those elaborated for the GREEN-Rgrid described in Malagó et al. [11].

SWAT was forced to use a predefined delineation of streams and watershed using a regular grid-cell and a river network of 5 arc-minutes of resolution (about 60 km² of grid cell area in the Po Basin). The imposed sub-basins and rivers in the Po consisted in 1232 regular polygons and segments. Consequently, hereafter we refer to grid-cells instead of sub-basins (Figure 1b). We chose to define sub-basins as regular grid-cells for several reasons. First, due to the rapid development of remote sensing systems, global spatial data (i.e., precipitation, soil characteristics, river network, population etc.) are available as raster format providing a more homogeneous information around the world. Consequently, different applications of SWAT can be easily compared, avoiding the uncertainty related to the use of different inputs. Second, the process of incorporating raster data into sub-basins instead of using directly grid-cells would require data transformation from a simple grid geometry to irregular polygons increasing the risk of loss of information and accuracy [26].

The digital elevation model (DEM) was retrieved from GTOPO30 [27] with a grid-cell of 30 arc seconds (approximately 1 km) that was rescaled at 100 m \times 100 m of resolution.

The land use map was derived from 100 m × 100 m raster map built from the combination of the GLOBCOVER 2009 map [28] and Spatial Production Allocation Model (SPAM) [29] that provides crop-specific physical area, harvested area, and yields for 42 crops. Data are available for the year 2005 (average of 3 years centered on 2005) for four production systems: irrigated high inputs, rainfed high inputs, rainfed low inputs, and rainfed subsistence.

Soil type and characteristics were defined using the Harmonized World Soil Database [30]. For each grid-cell we considered the dominant soil and we used the top soil layer data for a maximum of 1-m depth. The available water capacity of each soil was calculated using the pedotransfer function proposed by Rawls et al. [31] and the saturated hydraulic conductivity was calculated using the Saxton et al. [32] equation.

Based on the combination of land use, soils and slopes, the Po Basin was discretized into 6023 HRUs with areas ranging between 180 and 6000 ha.

The global HydroLakes database [33] was used for identifying lakes and reservoirs on the river network. At most one single lake was included in each grid-cell, using the area and volume parameters from the HydroLakes. In the Po River Basin, 25 major lakes were included for a total area of around 90,000 ha.

Daily precipitation was obtained from the global gridded MSWEP dataset at 0.25 degrees resolution [34]. Daily data for the other atmospheric forcing variables (temperature, solar radiation, wind speed and relative humidity) were obtained from ERA-Interim [35]. The whole dataset of climate data covers the period 1979–2012. To account for the increase in precipitation with elevation, that is typically observed in mountainous regions, four elevation bands were implemented [25].

The nutrient emissions from point sources were estimated based on urban and rural population, emission rates per person, the percentages of urban and rural population connected to wastewater treatment plants and their treatment technology level as explained in detail in Malagó et al. [11].

The water discharge from point sources was calculated using the amount of withdrawals for domestic uses provided by [36]. These values were also used as abstractions from deep aquifers in SWAT.

The daily nitrogen atmospheric deposition in each grid-cell was derived from a global map of 1 degree resolution of the World Data Centre for Precipitation Chemistry (http://wdcpc.org/).

The modelled crop management consists of planting, fertilization, irrigation, tillage and harvesting operations. The timing of management operations was implemented according to the heat units accumulated by crops [12]. The crop calendar was retrieved from the global dataset MIRCA2000 [37]. This dataset provides the start and end of the cropping period for 26 irrigated and rainfed crops on 402 global spatial units.

The accumulated heat units (HU) for each crop were calculated using the average daily temperature dataset in the period 1979–2012 [35], the duration of the growing season and the base temperature parameter provided by SWAT. Crop growth only occurs on those days where the mean daily temperature exceeds the base temperature. The heat units accumulated in the cropping period are the sum of the differences between average daily temperature and the base temperature.

The amount of manure, mineral fertilization, and irrigation were retrieved from Malagó et al. [11] for the year 2005 and kept constant through the simulation. One single application of N and P manure and N, P mineral fertilizers was used for each crop, managed grassland and fodder crop. For irrigated crops 10 applications of water were scheduled during the growing period. Two types of tillage (disk chisel and harrow 10 bar) were used before the application of manure. Table 2 reports an example of management for irrigated corn.

Scenario	Operation Code	Description	Month	Day	Application
	FERT MANN	Amount of N manure fertilizer application (0.99 ORGN)	10	14	112.2 kg/ha
	FERT MANP	Amount of P manure fertilizer application (0.99 ORGP)	10	14	24.7 kg/ha
	TILLAGE1	Disk Chisel (mulch Tiller) with depth of 150 mm and mixing efficiency of 0.55	10	15	0.
	TILLAGE2	Harrow 10 Bar Tine 36 Ft with depth of 25 mm and mixing efficiency of 0.2	10	24	
	PLANTING CORN	Beginning of plant growth	4	1	1787 HU
	FERT MINN	Amount of elemental N fertilizer applied to HRU	4	11	221.6 kg/ha
	FERT MINP	Amount of elemental P fertilizer applied to HRU	4	11	34.7 kg/ha
	IRRIGATION 1	Depth of irrigation water applied on HRU	4	22	12.6 mm
	IRRIGATION 2	Depth of irrigation water applied on HRU	5	7	12.6 mm
ne	IRRIGATION 3	Depth of irrigation water applied on HRU	5	22	12.6 mm
ili selii	IRRIGATION 4	Depth of irrigation water applied on HRU	6	6	12.6 mm
Bas	IRRIGATION 5	Depth of irrigation water applied on HRU	6	21	12.6 mm
	IRRIGATION 6	Depth of irrigation water applied on HRU	7	6	12.6 mm
	IRRIGATION 7	Depth of irrigation water applied on HRU	7	21	12.6 mm
	IRRIGATION 8	Depth of irrigation water applied on HRU	8	5	12.6 mm
	IRRIGATION 9	Depth of irrigation water applied on HRU	8	11	12.6 mm
	IRRIGATION 10	Depth of irrigation water applied on HRU	8	17	12.6 mm
	HARVEST	Harvoot and kill apprection stone the plant growth in the UPU	0	1	
	and KILL of CORN	That vest and kin operation stops the plant growth in the TIKO	9	1	
	HARVEST	Harvest and kill operation stops the plant growth in the HRU	3	15	
	and KILL RYE		-	•	110.01
	FERT MANN	Amount of N manure fertilizer application (0.99 ORGN)	3	20	112.2 kg/ha
	FERI MANP	Amount of P manure fertilizer application (0.99 ORGP)	3	20	24.7 kg/ha
	PLANTING CORN	Beginning of plant growth	4	1	1787 HU
	FERT MINN	Amount of elemental N fertilizer applied to HRU	4	11	199.5 kg/ha
	FERT MINP	Amount of elemental P fertilizer applied to HRU	4	11	34.7 kg/ha
	IRRIGATION I	Depth of irrigation water applied on HRU	4	22	12.6 mm
	IRRIGATION 2	Depth of irrigation water applied on HKU	5	22	12.6 mm
	IRRIGATION 3	Depth of irrigation water applied on HRU	5	22	12.6 mm
2	IRRIGATION 4	Depth of irrigation water applied on HRU	6	6	12.6 mm
<u>RI</u>	IRRIGATION 5	Depth of irrigation water applied on HRU	6	21	12.6 mm
0	IRRIGATION 6	Depth of irrigation water applied on HKU	7	6	12.6 mm
	IRRIGATION 7	Depth of irrigation water applied on HRU	7	21	12.6 mm
	IRRIGATION 8	Depth of irrigation water applied on HRU	8	5	12.6 mm
	IRRIGATION 9	Depth of irrigation water applied on HRU	8	11	12.6 mm
	IKRIGATION 10	Depth of irrigation water applied on HRU	8	17	12.6 mm
	and KILL of CORN	Harvest and kill operation stops the plant growth in the HRU	9	1	
	TILLAGE2	Harrow 10 Bar Tine 36 Ft with depth of 25 mm and mixing efficiency of 0.2	9	3	
	PLANTING RYE	The initiation of plant growth	9	4	800 HU

Table 2. Example of management operations for irrigated corn (grid-cell 403, HRU 5) as defined in SWAT for baseline and scenario CRP2 (see Section 2.4).

The annual irrigation (mm) for each irrigated crop was calculated applying a downscaling procedure based on the irrigation volume (m³) reported at country level for 26 crops by Siebert and Döll [38], the irrigated area in each cell retrieved from SPAM, and the difference between the potential evapotranspiration and precipitation as described in Malagó et al. [11].

The initial values of nitrate concentrations in the shallow aquifer required to initialize the model were derived putting in relation reported observed nitrate concentrations with environmental variables including climatic, soil, hydrological, and management data using a stepwise regression approach [39].

The simulation period covers 13 years from 2000 to 2012, in addition to 21 years of warm-up used to initialize model variables and allow processes to reach a dynamic equilibrium [40].

2.3. Calibration, Validation and Evaluation

The calibration of SWAT was performed following a cascade modelling approach starting from crop yield, then streamflow and finally nitrate concentration. The monitoring stations are located along the whole Po River as described in Table 3. These stations were selected since they provide important insights on model performance in estimating overall nutrient loads [19].

To assess the model performance for both calibration and validation, we used the percent bias (PBIAS) as recommended by Moriasi et al. [41].

PBIAS measures the tendency of the simulated data to be higher or lower than the observations. Values close to 0 indicate a lack of bias (neither underestimation nor overestimation). Positive and negative values indicate an overestimation and underestimation of the simulated data, respectively. We considered PBIAS values in the range of $\pm 25\%$ for monthly streamflow, nutrient concentrations and loads to be good and acceptable.

The modified coefficient of determination bR^2 was used in the calibration process for identifying the best parameter set for streamflow and nitrate concentrations. The percent bias and bR^2 were calculated using the R package "hydroGOF" [42].

2.3.1. Crop Yields

Crop yield calibration was based on the comparison of long-term average annual crop yields for the simulation period 2000–2012 with the annual values centered on 2005 provided by SPAM, and with the national statistics reported by FAOSTAT [43]. Since SWAT estimates dry crop yields, we converted SPAM and FAOSTAT yields from fresh to dry weights using crop moisture contents retrieved from Williams at al. [44] as described in Malagó et al. [11].

The crop calibrated parameters are reported in Table 4. In particular, the base temperature for bare, shrub, and grassland was set to 1 °C and to 3 °C for fodder crops. The radiation use efficiency was decreased from the default values to 5 and 20 kg/ha/MJ/m² for fodder crops and irrigated sugar beet, respectively. The parameters for rice were adjusted using the values proposed by Yang et al. [45].

2.3.2. Streamflow

The calibration of monthly streamflow was performed applying a regionalization technique of calibrated parameters in large river basins in Europe in previous SWAT studies, followed by an adjustment of the most sensitive parameters using the SUFI-2 method [46]. Times series of monthly streamflow for 8 monitoring stations along the Po River were divided into calibration and validation periods: 2005–2012 and 2000–2004, respectively.

In order to provide a more reliable evaluation of nitrate leaching into aquifer, only groundwater parameters were estimated by regionalizing values calibrated in previous large-scale applications in Europe: Spain and Scandinavian Peninsula [21], the Danube River Basin [22] and France [47]. The regionalization consists of a cluster analysis performed using the Self Organized Map (SOM) [48] and a similarity approach to transpose the calibrated parameters to all uncalibrated grid-cells [49]. These parameters, available for 61,439 cells in Europe, include: the groundwater delay (GW_DELAY, days), the baseflow alpha factor (ALPHA_BF, days), the threshold depth of water in the shallow

aquifer required for return flow to occur (GWQMN, mm), the groundwater transfer from the aquifer to the unsaturated zone coefficient (GW_REVAP), the threshold depth of water in the shallow aquifer for capillarity rise (REVAMN, mm) and the fraction of groundwater recharge to deep aquifer (RCHRG_DP).

The SOM is a modified artificial neural network characterized by unsupervised training that can project high-dimensional information into a low-dimensional array [50]. In the SOM, input samples are compared based on the variable characteristics and mapped onto vectors referred to as neurons and are positioned closed to each other on a matrix referred as a map. The neurons are thus grouped into clusters, where neurons are similar to each other. The cluster analysis was performed using the Ward's agglomerative hierarchical clustering method [51] that is based on a least-squares criterion, producing clusters that minimize within-cluster dispersion. In this study, training samples consist of 61,439 grid-cells characterized by the following features affecting the groundwater processes: elevation (m), slope (%), sand and clay content (%), organic matter content (%), the percentage of different classes of land cover, average annual precipitation (mm), average annual temperature (°C), average streamflow (m³/y), irrigated area (ha) and aquifer permeability (m/day).

The SOM method was applied to the training dataset and 13 clusters were obtained. The optimal number of clusters was selected using 30 indices based on the R NbClust package [52]. To assign all the remaining grid-cells to each cluster, the grid-cells of the test were associated to the SOM defined neurons using a predictive function based on the minimization of the Euclidean distance and consequently the cluster were identified based on the association of neuron-cluster.

Finally, inside each cluster the training grid-cells were used as donor to transpose the groundwater parameters in the uncalibrated grid-cells using a classification procedure based on hydrologic similarity [49].

After the regionalization, the transposed groundwater parameters were calibrated using the SUFI-2 algorithm in two steps that consist on: 1) changing all groundwater parameters in the range of +-50%, and the best parameter set was obtained among 100 combinations maximizing bR² between simulated and observed monthly streamflow; 2) reducing the set of groundwater parameters to the most sensitive ones, decreasing also the range for relative changes as reported in Table 4, and the final set of groundwater calibrated parameters were obtained from 100 simulations by maximizing bR² (Table 4).

2.3.3. Nitrate Concentrations

The nitrate concentrations were calibrated in 6 monitoring stations in the period 2005–2012 by changing the mineralization rate of active organic nitrogen and the nitrate half-life in the shallow aquifer. The best parameter set was obtained among 100 simulations by maximizing the bR² between simulated and observed monthly nitrogen-nitrates concentrations. The model was then validated in the same stations for the period 2000–2004. Finally, the model was evaluated comparing simulated and observed monthly loads for the whole period of simulation 2000–2012.

Description	Drained Area (km ²)	Distance from the Source (km)	# Data Entries for Streamflow (2000–2012)	# Data Entries for N-NO ₃ (2000–2012)
Po at Torino	7193	462	60	
Po at Pieve del Cairo	26,467	355	108	33
Po at Spessa	38,468	303	108	55
Po at Cremona Castelvetro	51,337	247	144	63
Po at Viadana	56,350	172	108	62
Po at Borgoforte	63,765	147	108	59
Po at Sermide	70,007	101	108	61
Po at Pontelagoscuro	72,396	65	144	
-	Description Po at Torino Po at Pieve del Cairo Po at Spessa Po at Spessa Po at Cremona Castelvetro Po at Viadana Po at Borgoforte Po at Sermide Po at Pontelagoscuro	DescriptionDrained Area (km²)Po at Torino7193Po at Pieve del Cairo26,467Po at Spessa38,468Po at Cremona51,337Castelvetro51,337Po at Viadana56,350Po at Borgoforte63,765Po at Sermide70,007Po at Pontelagoscuro72,396	DescriptionDrained Area (km²)Distance from the Source (km)Po at Torino7193462Po at Pieve del Cairo26,467355Po at Spessa38,468303Po at Cremona51,337247Castelvetro51,337247Po at Viadana56,350172Po at Borgoforte63,765147Po at Sermide70,007101Po at Pontelagoscuro72,39665	DescriptionDrained Area (km²)Distance from the Source (km)# Data Entries for Streamflow (2000-2012)Po at Torino719346260Po at Pieve del Cairo26,467355108Po at Spessa38,468303108Po at Spessa51,337247144Castelvetro51,350172108Po at Viadana56,350172108Po at Sermide70,007101108Po at Sermide70,007101108

Table 3. Characterization of monitoring stations along the Po River (# is the number of data entries).

Process	Parameter and Input File	HRUs	Description	Range	Calibrated Value
	T_Base.crop	Bare, shrub and grassland	Minimum/base temperature for plant growth	0.12	1
		Fodder crop	Minimum/base temperature for plant growth	0–12	3
Plant growth		Fodder crop	Radiation use efficiency	10-90	5
r lant growth	BIO_E.crop	Irrigated sugar beet	Radiation use efficiency	10–90	20
		Rice	Radiation use efficiency	10–90	25
	HVSTI.crop	Rice	Harvest index	0.01-1.25	0.54
	FRGRW2.crop	Rice	Fraction of the plant growing season corresponding to the 2nd point on the optimal leaf area development curve	0–1	0.51
	LAIMX1.crop	Rice	Fraction of the maximum leaf area index corresponding to the 1st point on the optimal leaf area development curve	0–1	0.28
	LAIMX2.crop	Rice	Fraction of the maximum leaf area index corresponding to the 2nd point on the optimal leaf area development curve	0–1	0.99
	ALPHA_BF.gw	all	Baseflow alpha factor	-0.5-0.5 (relative)	0.045 (relative) ¹
Baseflow generation	GW_DELAY.gw	all	Groundwater delay time	-0.5-0.5 (relative)	–0.497 (relative)
	RCHRG_DP.gw	all	Deep aquifer percolation fraction	-0.5-0.5 (relative)	0.377 (relative)
Nitrogen cycle	HLIFE_NGW.gw	all	Half-life of the nitrate in shallow aquifer	100-1000	1007.5
i villogen cycle	CMN.bsn	all	Rate factor for humus mineralization of active organic nutrients	0.0001-0.003	0.001465

Table 4. Description of calibrated parameters involved in the calibration with their range before and after calibration.

¹ "relative" means that the existing value is multiplied by (1 + the given value).

2.4. Scenario Analysis

Different basin management scenarios were developed for assessing the efficiency of mitigation strategies for nitrate reduction in the Po watershed. The strategies focused both on nutrient reduction at the source (mineral and manure fertilizers) and on crop management with the introduction of a winter catch crop during the fallow period following corn harvest.

The nitrogen mitigation strategies were formulated in seven management scenarios of agricultural practices (Table 5) that were implemented in cropland area (16% of the whole watershed). The selected crop area consists of 2208 HRUs with areas ranging from 180 to 5200 ha.

The first scenario (NMIN) consists of a reduction of mineral fertilizer application in agricultural HRUs ensuring that the annual crop yield would not decrease more than 5% from the baseline in order to guarantee the farmers income. Scenarios MAN170 and MAN250 were developed to mimic the restrictions imposed by the Nitrates Directive [4]. In NVZs, the Directive limits the use of manure to 170 kg/ha, or 250 kg/ha in case of derogation. Other scenarios tested the use of cover crops after the harvesting of corn, the main spring-summer crop in the basin. Cover crops were implemented in 730 HRUs.

Cover crops protect against erosion between two corn growing seasons; they build up the organic matter in the soil following their killing [53], and they assimilate nitrate, reducing leaching during the winter. Three scenarios of cover crops were implemented. The first (CRP1) uses rye as cover crop. The second (CRP2) uses rye as cover crop after harvesting the corn, for which the mineral fertilizer application is reduced, and an example of management is reported in Table 2. The third (CRP3) is the same of CRP2, but red clover is used instead of rye. Red clover provides many benefits such as fixing nitrogen to meet the needs of the following crop, protecting soil from erosion, competing with weeds, as well as supplying forage [54]. Finally, a mixed scenario was tested combining the strategies implemented in other scenarios: (i) reduction of mineral nitrogen fertilizer in all crop fields (2208 HRUs) (NMIN); (ii) manure application below 170 kg N/ha (MAN170); (iii) use of red clover as cover crop after harvesting corn (CRP3).

Each of the seven scenarios of Table 5 was simulated for the period 2000–2012 and compared with the baseline simulation results (REF).

Scenario Acronym	Description	#HRU Affected	Area (km ²)
NMIN	Strategic reduction of mineral fertilizer application in each HRU limiting the change in annual crop yield from baseline below 5%	2208	12044
MAN170	Restriction of manure application to maximum 170 kg N/ha/y	71	332
MAN250	Restriction of manure application to maximum 250 kg N/ha/y	9	40
CRP1	Planting rye after harvesting corn and harvesting it before planting corn.	730	5503
	Strategic reduction of mineral fertilizer application in each HRU with corn (as		
CRP2	scenario NMIN) and planting rye as cover crop (as scenario CRP1) after	730	5503
	harvesting corn		
CRP3	Strategic reduction of mineral fertilizer application in each HRU with corn (as scenario NMIN) and planting red clover as cover crop after harvesting corn	730	5503
COMB	Combination of scenario NMIN, MAN170 and CRP3	2208	12044

Table 5.	Scenario	description	s (# is the nu	mber of HRUs)
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3. Results

3.1. Analysis of Model Calibration and Validation

3.1.1. Crop Yields

Crop yields were calibrated considering the whole period of simulation 2000–2012. The results were satisfactory as the predicted annual crop yields compared well with both SPAM and FAOSTAT values (Figure 2). Relatively large overestimations were observed for sorghum, potatoes under highly intensive management and vegetables (HSOR, HPOT and e.g., HVEG, see Table A1 in Appendix A for the description).

The annual variability of yields of dominant crops, low intensive corn (LMAI) and irrigated corn (IMAI), were well captured as shown by the strong correlation between SWAT and FAOSTAT values (Table 6). The predicted yields for wheat exhibited low correlation with the values reported by FAO, and the standard deviation of wheat annual yields was 1.2 ton/y and 0.35 ton/y respectively for SWAT and FAOSTAT. This can be explained considering that FAO yields sum irrigated and rainfed productions. Irrigated rice yields resulted negatively correlated with annual FAO yields. The simulated SWAT values are strongly correlated with water stress (in years where water stress increases, irrigated rice yields decreased), while FAO yields follow an opposite trend.



Figure 2. Comparison of simulated and observed annual crop yields from SPAM (**a**) and FAOSTAT (**b**) in the period 2000–2012. The acronyms of crop names are reported in Table A1 in Appendix A.

Table 6. Pearson correlation coefficient (r) calculated between SWAT simulated annual crop yields and FAOSTAT in the period 2000-2012 for the main crops in the basin.

Crop Code	Crop Name	Area (ha)	r
LMAI	Corn under low intensive management	3717	0.58
IMAI	Irrigated corn	1782	0.70
HWHE	Wheat under highly intensive management	1748	-0.06
IRIC	Irrigated rice	1740	-0.60

3.1.2. Streamflow and Nitrates

The performances of SWAT in simulating monthly streamflow are satisfactory both for calibration and validation (Table 7 and Figure 3). The PBIAS (%) was good for streamflow and N-NO₃ concentrations according to the ratings proposed in Moriasi et al. [41]. The PBIAS% calculated between the observed and simulated monthly nitrate loads resulted also very good (Figure 3 and Table 7). Visual appraisal of monthly streamflow, concentrations and loads in Figure 4 confirmed that monthly variations were well captured and that peaks are well reproduced.

The residuals (simulated minus observed values) in six stations along the Po River were well centered on zero (Figure 5). However, some underestimations of simulated nitrate concentration can be observed in the lower stations near the mouth, and in particular for station Borgoforte at 147 km from the mouth.

Variable	# Monitoring Stations/Data Entries	Simulation Period	PBIAS (%)
Monthly stroomflow	8/408	Calibration (2005-2012)	3.7
Wonting streamnow	8/480	Validation (2000–2004)	-10.8
Monthly N NO. concentrations	6/244	Calibration (2005–2012)	12
Monthly N-NO ₃ concentrations	6/89	Validation (2000–2004)	-4.1
	6/244	Calibration (2005–2012)	14.1
Monthly N-NO ₃ loads	6/89	Validation (2000-2004)	-19.4
	6/333	Evaluation (2000–2012)	4.3

Table 7. Description of calibrated and validated variables (# = number; N-NO₃ = nitrogen nitrates) and model performance.



Figure 3. Comparison of simulated (SIM) and observed (OBS) monthly streamflow (m^3/s) , N-NO₃ concentrations (mg/L) and loads (kg/month) in the calibration (CAL, upper three graphs) and validation (VAL, lower three graphs) periods.



Figure 4. Monthly time series of streamflow (**a**,**d**), nitrogen-nitrate concentrations (**b**,**e**) and monthly loads (**c**,**f**) observed (red lines and points) and simulated by SWAT (black line) at two selected gauging stations across the Po River.



Figure 5. Box plots of residuals (simulation-observation) of monthly streamflow (**a**), N-NO₃ concentrations (**b**), loads (**c**) and specific loads (**d**) along 6 stations from source to mouth (left to right) of the Po River.

3.1.3. Annual Water and Nitrogen Balance

Figure 6 shows the long-term mean annual water and nitrogen balance for the entire Po River Basin (74,600 km²) as simulated by SWAT for the period 2000–2012. It was estimated that 47% (487 mm) of precipitation (PCP, 1036 mm) was lost through evapotranspiration (ET) and 2% as percolation in the deep aquifer, and 51% was discharged in the stream (water yield, WYLD, 528 mm). Surface runoff (SR) and baseflow from shallow aquifer (BF_S) were the main pathways of water losses.

Regarding the nitrogen balance, the diffuse inputs were estimated at about 91 kg/ha consisting of 27.2 kg/ha mineral fertilizer, 33.4 kg/ha of manure, 17.9 kg/ha of nitrogen fixation and 12.5 kg/ha of atmospheric deposition. Point sources amounted to about 5.7 kg/ha. The nitrogen removed by crops and the nitrogen lost in the soil were estimated to be about 40% and 20% of nitrogen inputs, respectively. About 7% (5.9 kg/ha) of total inputs were emitted to the river while 33% (30.8 kg/ha) of total inputs leached to the aquifer. The largest contributor of the emissions to the rivers was the baseflow with about 13.8 kg/ha. The total nitrogen emissions to the river were estimated at 19.8 kg/ha, which together with point sources contributed to a load of about 25.5 kg/ha.

Diffuse and point sources were responsible of 78% and 22% of the total nitrogen load in the Po River. These estimations were comparable to those reported by other studies in the Po Basin [19,20]. In these studies, the diffuse sources were estimated to be around 70% and 60%, respectively, while the contribution of point sources amounted to about 30% and 40%, respectively. In particular, Palmeri et al. [19] estimated a groundwater contribution of 13.7 kg N/ha and surface runoff load of 0.65 kg N/ha.

The long-term annual average of nitrate loads at Pontelagoscuro were 115,000 ton-N/y, 93,460 ton-N/y, and 78,032 ton-N/y for the periods 2000–2012, 2003–2008 and 2003–2007, respectively. These values are consistent with those provided by other authors [11,19,20,55] (Table 8), as well as with the observations monitored at Sermide, the nearest station to Pontelagoscuro.



Figure 6. Long-term mean annual water, mm, (**a**) and nitrogen, kg/ha, (**b**) balances for the entire Po River Basin for the period 2000–2012. In (**a**): PCP precipitation, ET evapotranspiration, INF infiltration, SR surface runoff, LF lateral flow, BFS groundwater from shallow aquifer, BFD groundwater from deep aquifer. In (**b**): NAPP nitrogen applied as fertilizer, NMIN nitrogen mineral fertilizer, NMAN nitrogen manure fertilizer, NFIX nitrogen fixation, NRAIN nitrogen in atmospheric deposition, Nyld nitrogen removed by crop yields, SRN nitrogen transported via surface runoff, LFN nitrogen transported via surface runoff, LFN nitrogen transported via groundwater, Nleach nitrates that leached into aquifer, NPS nitrogen from point sources directly discharged into rivers, Nloads nitrogen loads into rivers.

Reference	Model	Period	N-NO ₃ (ton/y)
		2000-2012	115,000
Our study	SWAT	2003-2008	93,460
		2003-2007	78,032
Salvetti et al. [20]	QUAL2E/SWAT	1985-2001	107,000
Palmeri et al. [19]	MONERIS	1996-2000	123,482 *
Naldi et al. [55]	-	2003-2007	85,000
Malagó et al. [11]	GREEN-Rgrid	2003-2007	86,295
Long term average annual load at Sermide	-	2003-2008	93,462

Table 8. Comparison N-NO₃ SWAT annual estimations at Pontelagoscuro with other studies and observations at Sermide, the nearest station to Pontelagoscuro with observations.

* DIN dissolved inorganic nitrogen.

3.2. Analysis of Scenarios of Agricultural Practices

Table 9 shows the potential effects of different management strategies on nitrate fate in cropland areas for the period 2000–2012.

An analysis of the scenarios suggests that a targeted mineral fertilizer reduction of 23% from the baseline (NMIN) could decrease nitrate leaching and nitrogen emissions by 24% and 21%, respectively, with limited impact on crop yield. In particular, the main effect was observed in the reduction of nitrates transported via groundwater (BFN: 24% of reduction with respect to baseline) followed by nitrogen transported via lateral flow (LFN: 14%) and surface runoff (SRN: 13%). The highest reduction of organic nitrogen transported via sediment to river (ORGN) was observed in the scenarios of cover crops (from 33% of reduction of scenario CRP1 to 40% of scenario CRP3) explained by the decrease of sediment yield (SYLD) by about 50%.

The introduction of winter cover crops has a significant impact on nitrate reduction, and a limited impact on the water balance as reported in other studies [56–58]. Concerning the hydrology, we observed slightly lower water yields and higher evapotranspiration compared to the baseline. Rye and red clover cover crops reduced water yields in the cropland area from 301 mm (baseline) to 287 and 289 respectively, while evapotranspiration increased from 600 mm of baseline to 614 and 612 respectively.

The effect of winter cover crops in reducing nitrate leaching and nitrogen emissions is noticeable, in particular when coupled with a targeted reduction of mineral fertilizers. CPR2 scenario decreased nitrate leaching (Nleach) and nitrogen emissions (Nem) by 8% and 6% with respect to CPR1.

Red clover had additional benefits with respect to rye by reducing sediment yields by more than 50%, increasing the amount of nitrogen in the soil and consequently leading to an increase of crop yields in the Po River by about 18%. This was also pointed out by several studies as described in Marcillo at al. [59].

Figure 7 shows the changes of crop yields and nitrogen leaching for the main four crops in the basin in the tested scenarios. The effect of cover crops in scenario CRP3 on rainfed (LMAI) and irrigated corn (IMAI) is showing an increase of crop yields from the baseline by about 25% and 20%, respectively and a decrease of nitrate leaching by about 60% and 50%, respectively.

It should be noted that, albeit winter cover crops scenarios were implemented only on 5500 km² (about 46% of crop land area in the basin), we obtained larger reductions of nitrogen leaching and emissions than those obtained in the more extensive NMIN scenario.

As expected, manure reduction scenarios are less beneficial in terms of N reduction in the river, but they bring significant local impacts (Figure 8), because the HRUs with N applications greater than 170 and 250 kg/ha were respectively only 71 and 9 covering respectively 332 km² and 40 km².

The mixed effect of red clover implementation after harvesting corn, with the targeted reduction of mineral fertilizers and the limitation of nitrogen manure to 170 kg/ha (COMB) had the highest impact on nitrogen reduction, maximizing the reduction of sediment yields and maximizing crop yields (Table 9, Figures 7 and 8).

We have also observed that COMB and NMIN scenarios have the largest impacts in the reduction of concentrations and loads in the Po River (Figure 9), improving water quality all along the river from source to mouth.

The evolution of the nitrate concentration along the Po River is shown in Figure 9. It is noteworthy that along the Po River three concentrations peaks were simulated before the junction of Dora Riparia with Po at Turin (km 473 from the mouth), before the confluence of the Ticino River (330 km from the mouth) and Adda River (278 km from the mouth). These peaks reached the highest values during June–July in the baseline simulation, exceeding 25 mg/L near Turin (Figure A1).

Our results capture the degree of groundwater nitrate contamination in shallow and deep aquifers in the western Po plain between Turin and Cuneo cities. In those areas, 37.6% of agricultural areas are NVZs, with 50% of the monitored points with nitrate concentration between 25 and 50 mg/L, and 24% larger than 50 mg/L [18]. Consequently, as the groundwater flows into the Po River before Turin [60], large amounts of nitrate are concentrated there (Figures 9, A1 and A2).

The main sources of nitrate contamination in this area are mineral fertilizers and manure [18]. The COMB scenario predicts a substantial reduction of nitrates concentration in this part of the Po River, suggesting that a combination management option may be an efficient strategy to reduce nitrate contamination.

In other sections of the Po River the simulated concentrations remain quite constant (Figures A1 and A2), albeit several tributaries, such as the Oglio River, drain areas with large nitrogen surplus from agriculture. In particular, Bartoli et al. [61] found that the nitrate concentrations in the Oglio River, in its tributaries, in groundwater and springs, are greatly reduced by the denitrification in wetlands that are hydraulically connected with the river network.

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Table 9. Specific nutrient loads per scenarios in cropland HRUs (12,044 km², 16% of the whole basin). In parenthesis the percentage of reduction (negative values) or increment (positive values) respect the baseline (REF).

										Scen	arios						
	Components	Units of Measures	REF	NN	4IN	NMA	N170	NMA	N250	CR	RP1	CI	RP2	CI	RP3	CO	МВ
NAPP	Mineral fertilizer and manure application	kg N/ha	199.28	165.23	(-17%)	198.28	(-1%)	199.18	(0%)	199.28	(0%)	184.2	(-8%)	184.2	(-8%)	164.24	(-18%)
NMIN	Mineral fertilizer	kg N/ha	149.07	115.03	(-23%)	149.07	(0%)	149.07	(0%)	149.07	(0%)	134	(-10%)	134	(-10%)	115.03	(-23%)
NMAN	Manure	kg N/ha	50.2	50.2	(0%)	49.2	(-2%)	50.1	(0%)	50.2	(0%)	50.2	(0%)	50.2	(0%)	49.2	(-2%)
NFIX	Nitrogen fixation	kg N/ha	3.21	3.21	(0%)	3.23	(1%)	3.21	(0%)	3.21	(0%)	3.21	(0%)	21.49	(569%)	21.66	(575%)
NRAIN	Nitrogen in atmospheric deposition	kg N/ha	13.4	13.4	(0%)	13.4	(0%)	13.4	(0%)	13.4	(0%)	13.4	(0%)	13.4	(0%)	13.4	(0%)
NUP ¹	Nitrogen uptake in the soil	kg N/ha	185.38	166.29	(-10%)	185.19	(0%)	185.37	(0%)	209.07	(13%)	193.89	(5%)	217.28	(17%)	210.99	(14%)
Nleach	NO ₃ leached into the aquifer	kg N/ha	125.4	95.47	(-24%)	124.71	(-1%)	125.33	(0%)	109.65	(-13%)	98.83	(-21%)	97.19	(-22%)	78.63	(-37%)
Nem	Nitrogen emissions	kg N/ha	66.51	52.64	(-21%)	66.25	(0%)	66.48	(0%)	55.86	(-16%)	51.59	(-22%)	50.7	(-24%)	41.7	(-37%)
SRN	Nitrogen transported via surface runoff	kg N/ha	1.24	1.08	(-13%)	1.24	(0%)	1.24	(0%)	1.24	(0%)	1.13	(-9%)	1.16	(-6%)	1.09	(-12%)
LFN	Nitrogen transported via lateral flow	kg N/ha	0.07	0.06	(-14%)	0.07	(0%)	0.07	(0%)	0.06	(-14%)	0.06	(-14%)	0.06	(-14%)	0.05	(-29%)
ORGN	Organic nitrogen transported with sediment	kg N/ha	9.57	9.2	(-4%)	9.55	(0%)	9.57	(0%)	6.39	(-33%)	6.2	(-35%)	5.78	(-40%)	5.68	(-41%)
BFN	NO ₃ transported via groundwater	kg N/ha	55.63	42.3	(-24%)	55.39	(0%)	55.6	(0%)	48.17	(-13%)	44.2	(-21%)	43.7	(-21%)	34.88	(-37%)
SYLD	Sediment yield	ton/y	6.25	6.26	(0%)	6.25	(0%)	6.25	(0%)	3.03	(-52%)	3.04	(-51%)	2.93	(-53%)	2.93	(-53%)
YLD	Crop yield	ton/y	5.97	5.78	(-3%)	5.96	(0%)	5.96	(0%)	6.53	(9%)	6.39	(7%)	7.07	(18%)	7.01	(17%)

¹ Plant uptake of N in the soil. This is the result of the processes involved in the nitrogen cycle in the soil (mineralization, decomposition, nitrification, ammonia volatilization and denitrification). Instead, Nyld (Figure 6) is the nitrogen removed with the crop yields, thus it represents the effective amount of nitrogen losses from the system by plants.



Figure 7. Changing of total nitrogen applied as fertilizer, crop yields, and nitrogen leaching for four dominant crops in the basin per scenarios (LMAI: low intensive corn, IMAI: irrigated corn, HWHE: highly intensive wheat, IRIC: irrigated rice).



Figure 8. Spatial analysis of distribution of long-term mean of nitrogen emissions (kg/ha), nitrogen leached into aquifer (kg/ha) and nitrate concentration leached into aquifer for the baseline (REF) and scenarios NMIN, MAN170, CRP3 and COMB.



Figure 9. Comparison of simulated long-term mean annual N-NO₃ concentrations and loads in the period 2003–2008 (where observations are concentrated) as function of the distance from the mouth. The black dots represent the long term mean annual observations calculated in the period 2003–2008.

4. Discussion and Conclusions

The global increase in the use of nitrogen synthetic fertilizers and manure over the last several decades has led to a degradation of water quality, especially in agricultural areas.

In Europe, several EU policy measures exist for controlling nitrogen emissions in the environment. In particular, the main objective of the Nitrates Directive is to "reduce water pollution caused or induced by nitrates from agricultural sources and prevent further such pollution". This directive forces member states to set up monitoring systems, to designate vulnerable zones, and to activate protection plans that must contain mandatory measures related to the definition of a code of good agricultural practices, including balanced N fertilization, and to limit the amounts of animal manure (170 kg/ha/y) applied to land.

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Italy transposed the directive in national legislation in 1999 (D.Lgs. 152/99). The national legislation transferred responsibility for identifying vulnerable zones to the regional authorities (Regions). The Po River Basin was, and still is, particularly problematical, with its shallow aquifers containing generally high levels of nitrates in the Cuneo–Turin plain, Alessandria area, in the north of Milan and in the Emilia–Romagna plain [16]. This is confirmed by our findings that highlight how current land management, after 20 years from the implementation of the Nitrates Directive, still results in significant vulnerability of the Po valley to nitrate leaching from diffuse sources and requires further mitigation measures (Figure 8, Figure A2).

The scenarios tested with SWAT show that the implementation of good agricultural practices could lead to a significant decrease of nitrate losses both to aquifers and rivers. We show that a reduction by as much as 37% of nitrate losses (COMB scenario) could be obtained with limited effects on crop production. It must be noted that this reduction will not affect the eutrophication of the Northern Adriatic Sea since it is mostly phosphorus limited [62]. However, it will strongly affect the quality of both stream and groundwater, improving also the good ecological status of surface water bodies.

Simulated nitrate leaching in the aquifers and emissions to surface waters were effectively reduced applying a targeted reduction of fertilizers (NMIN) and using winter cover crops (CPR1, CRP2, CRP3). These results agree with De Maio et al. [16], who suggested reducing agricultural nutrient pollution in Europe by moving towards agricultural systems where the input (manure and mineral fertilizers) is commensurate with the requirements of the crops (output). However, the sole reduction of nitrogen fertilizers does not cope with the problem of soil erosion losses due to tillage and occurring in the period where no crop is growing. Instead, cover crops proved to be an effective strategy for controlling sediment yield and for reducing nitrate leaching and emissions by 53%, 22% and 24% respectively (scenario CRP3, Table 9). Cover crops are shown to be the most effective practice in the Po River Basin land types that can be characterized as deep and permeable soils in the classification by Rittenburg et al. [63]. In this environment, cover crops increase the residence time of nitrates in the soil layers, increase plant nitrogen uptake, reduce soil erosion and nutrients transported via sediments, and increases soil carbon content [64].

The scenarios related to the limitation of manure application as required by the Nitrates Directive were not effective for the whole watershed as the spatial extent of implementation is extremely limited. With scenario MAN170 we can reduce the manure application on cropland by 2% (1200 ton of N manure; 36 kg/ha), while with scenario MAN250 by 0.2% (118 ton of N manure; 3.5 kg/ha) (Table 9). Similar conclusions were reported by De Wit et al. [65], who highlighted that the Nitrates Directive implementation resulted in significant local improvements of environmental conditions, but not in substantial reductions of N and P loads in large European river basins. It must be noted that our scenarios simulated the reduction of manure application assuming that the unused manure was lost. A better management of large quantities of manure available in limited areas, such as manure distribution networks, would allow the reduction of mineral input requirements, thus ensuring economic sustainable yields, and to limit pollution from diffuse sources. Solutions to manage the excess of manure could include i) the transfer outside the farm; ii) transformation or treatment (e.g., methanisation, composting or biological treatment); iii) burning for cement works [66]. These options can provide additional income for the farmers.

In this assessment, we showed that a reduction of nitrate losses could be achieved without affecting the economic sustainability of farmers. We further show that a combination of both nitrogen application reduction and the introduction of catch crops in rotation with typical crops of the Po River Basin could reduce nitrate losses into aquifers by as much as 20% (CRP3 scenario). The use of catch crops is particularly efficient considering that the nitrate losses in the Po watershed come mostly from the shallow aquifers. Thus, reducing nitrate leaching is particularly recommended in the flat part of the watershed. Winter crop cover strategy is more efficient in the hilly part of the watershed.

The use of the SWAT model is extremely efficient in identifying the types of measures depending on the local conditions.

Future work will focus in assessing how the proposed measures will perform under a changing climate. Indeed, expected climate change in the Mediterranean will include a decrease of precipitation during spring and summer and increase in fall and winter, while temperatures will increase throughout the year [67]. Crop management will be affected: an increase of irrigation is expected, while the increase of precipitation during fall and winter might yield large nitrate leaching. The increasing temperature will also affect the nitrogen cycle, leading to an increase of mineralization. Additional measures might have to be put in place to offset these expected changes.

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Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

Crop Code	Crop Name	Management Type
HBAR	Barley	Highly intensive
HMAI	Corn	Highly intensive
HOOI	Other oil crops	Highly intensive
HOPU	Other pulses	Highly intensive
HPOT	Potato	Highly intensive
HRIC	Rice	Highly intensive
HSOR	Sorghum Hay	Highly intensive
HSOY	Soybean	Highly intensive
HSUB	Sugarbeet	Highly intensive
HSUN	Sunflower	Highly intensive
HTEM	Temperate fruits	Highly intensive
HTRO	Tropical fruits	Highly intensive
HVEG	Vegetables	Highly intensive
HWHE	Wheat	Highly intensive
IMAI	Corn	Irrigated
IRES	Other crop	Irrigated
IRIC	Rice	Irrigated
ISUB	Sugarbeet	Irrigated
ITEM	Temperate fruits	Irrigated
ITOB	Tobacco	Irrigated
ITRO	Tropical fruits	Irrigated
IVEG	Vegetables	Irrigated
LMAI	Corn	Low intensive
LOCE	Other Cereal	Low intensive
LTEM	Temperate fruits	Low intensive
LVEG	Vegetables	Low intensive
STEM	Temperate fruits	Subsistence
SVEG	Vegetables	Subsistence

Table A1. SWAT crop code and description.





Figure A1. Monthly analysis of simulated N-NO₃ concentrations in the period 2000–2012 as function of the distance from the mouth. The horizontal grey lines represent the limits of 5.6 mg N/L (or 25 mg/L) and 11.3 mgN/L (or 50 mg/L).



Figure A2. Spatial distribution of total nitrogen applied (kg/ha) and long term average of annual N-NO₃ concentrations (mg/L) in the period 2000–2012 for baseline REF (**a**) and scenario COMB (**b**).

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