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Integrated modelling to assess N pollution swapping in slurry amended soils

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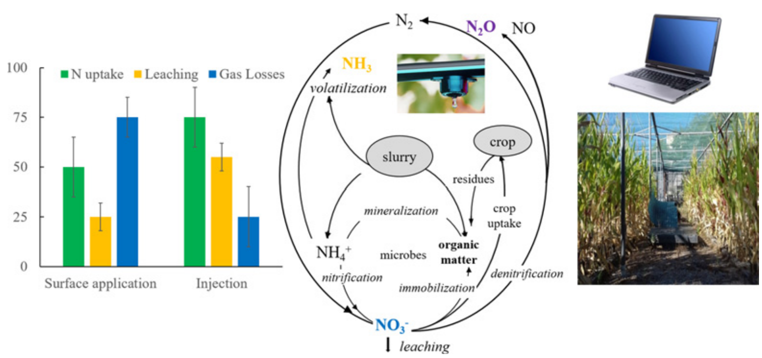
HIGHLIGHTS

- N pollution swapping might be a risk when compartment targeted solutions are proposed.
- N fluxes to soil, air, and water were assessed by integrating modelling and field experiments.
- We estimated the EFs lower than the IPCC default, and with high inter-annual variability.
- Recommendation of slurry injection as best available technique need to be reconsidered.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work, it was hypothesized that through modelling it is possible to overcome the constraints that arise in the quantification of N pollution swapping associated to slurry application practices when using individual experimental data. For this, environmental N losses were assessed under two methods of dairy slurry application to a double cropping system (rainfed oats (*Avena strigosa*)/irrigated maize (*Zea mays*)) in two different soils. An integrated experimentation and modelling approach was applied using the RZWQM2 model. The model was first tested using four years of experimental data concerning N fluxes to/from different environmental compartments (soil mineralization, N gas emissions, and N leaching). The model estimated emissions with overall efficiencies of ~70% and r^2 ~ 0.75. Total N losses were higher for surface band application (95.4 and 40.2 kg ha^{-1} for the sandy and sandy loam soils, respectively). However, when slurry was injected, nitrate leaching considerably increased (by 107 and 64% for the sandy and sandy loam soils, respectively), even though gas emissions were minimized. This N swapping among path losses requires targeting of the N mitigation measures to the environmental compartment showing the highest vulnerability. Generally, the estimated emission factors (EFs) were lower than or equal to (slurry injection in the sandy loam soil) the IPCC default. The values showed high variability, reinforcing the need to use agricultural system specific EFs. The methodologies used in this study, focused on scenario analysis, can support policy as they can be used to set up integral strategies to decrease N emissions from livestock farming systems, taking into account possible synergies and antagonisms produced by the measures among NH_3 and N_2O emissions and NO_3^- leaching.

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1. Introduction

Agriculture intensification and the consequent increase in nitrogen (N) fertilizer usage, together with the industrialization of livestock production, have generated large amounts of N-rich manures, namely slurry (Ilea, 2009; Malek et al., 2018). This has led to considerable N surpluses and mineral N accumulation in soils, contributing to increased losses to the different environmental compartments - such as water bodies contamination with nitrate (NO_3^-) and N emissions to the atmosphere, including ammonia volatilization (NH_3) and direct and indirect nitrous oxide (N_2O) emissions (Oenema et al., 2011; Chadwick et al., 2011; Bittman et al., 2014; FAO, 2017).

Ammonia is an important air pollutant contributing to eutrophication and acidification of ecosystems and to respiratory diseases (Sutton and Fowler, 2002; Erisman et al., 2008). Its anthropogenic emissions originate mainly from agricultural activities, fertilizer, and manure management (Bittman et al., 2014). The atmospheric concentration of N_2O, a powerful greenhouse gas, has increased at a rate of 0.73 ppb year^{-1} during the past three decades (IPCC, 2013). Agriculture is responsible for 60% of global anthropogenic N_2O emissions (Bhatia et al., 2010), primarily due to the use of synthetic fertilizers and manures (Davidson, 2009). Excessive nitrate emissions to water bodies are still occurring throughout Europe despite the large set of legislation (Bouraoui and Grizzetti, 2014), e.g. the Water Framework Directive (WFD) (2000/60/EC) and the Nitrate Directive (ND) (Council Directive 1991/676/EEC). These directives require European Union (EU) countries to achieve certain results regarding water bodies' quality and quantity, but leave them free to choose how to do so. EU countries must adopt measures to incorporate them into national law in order to achieve the objectives set by the directive. The WFD and the ND were transposed into Portuguese legislation by the Law of Water (Decree-Law 130/2012) and the Ordinance 259/2012, respectively. The consequences of excessive nitrates for water quality and human health are well reported (Grizzetti et al., 2011). The issue is still a problem in areas where crop fertilization is strongly based on animal manures, in particular when large amounts of animal slurry are applied to soils (Fan et al., 2017; Giola et al., 2012; Cameira et al., 2019a). Cattle manure, namely cattle slurry (liquid manure) is widely used as organic fertilizer in dairy farms since it provides an important input of nutrients (N, P and K to soil) as well as some organic matter. It is a solution to minimize the use of mineral fertilizers and to promote the recycling of nutrients inside the farm. In the northern part of Portugal, 98% of the slurry produced in dairy farms is applied as a fertilizer in the farm, while in the rest of the country the percentage decreases to 82% (INE, 2009). The cropland amended with slurry corresponds to 4.3 and 0.6% of the utilized agricultural area, respectively. Nevertheless, we can relate the use of slurry to the evolution of the livestock population. As shown in Cameira et al. (2019a), at the EU level, there was a decrease in cattle and pig populations between 2005 and 2016 (Eurostat, 2018). Only 10 countries presented an increase in the cattle population and only six countries had an increase in their pig population. Nationally, for the same period, Portugal had increases of 9 and 11% for the total number of cattle and pigs, respectively, suggesting an increase in the areas amended with slurry since the last national survey (2009).

However, cattle slurry application to soil leads to significant ammonia emissions. Hence, a large number of solutions were developed to minimize such N losses. Among them, slurry injection at 5–10 cm in soil is the recommended solution (compulsory in some countries). However, other solutions as band application or shallow injection are also used in many farms.

Application of synthetic fertilizers, manures, and other organic materials has to comply with policy measures dealing with emissions to air, soil, and water. This is a difficult task since no single mitigation method is able to reduce the concentrations of all pollutants simultaneously (Agostini et al., 2010; Quinton and Stevens, 2010). Thus, pollution swapping among environmental compartments might be a risk when new solutions are proposed, namely between NO_3^- leaching and N_2O or/and NH_3 emissions, requiring a holistic approach to the N diffuse pollution issue. Indeed, shallow incorporation and injection of slurry are presented as alternative mitigation measures to surface application (Bittman et al., 2014) since they have shown to decrease NH_3 volatilization, but they have the potential to increase N_2O emissions (Duncan et al., 2017) as well as NO_3^- leaching (Cameira et al., 2019b).

European Union Member States are required to report the status of their various N emissions. The Intergovernmental Panel on Climate Change (IPCC) provided a framework for the calculation of N_2O emissions from different sources at the national level (IPCC, 2006), based upon emission factors (EFs). In the absence of specific values, the IPCC recommends the use of a default EF of 0.01 kg N_2O-N per kg of applied N, independent of the fertilizer type, application technique, and land use (IPCC Tier I methodology, IPCC, 2006). However, the factors determining emissions vary in space and time and interact with each other in complex ways (Wagena et al., 2017). In particular, the Mediterranean regions present specificities that require the refinement of this EF estimate (Cayuela et al., 2017); for instance, the coexistence of irrigated and rainfed crops, soils with neutral to alkaline pH, and low concentrations of organic carbon (C). Furthermore, the soils are rarely exposed to freezing, unlike those in the countries where most EFs were determined (Tenuta and Sparling, 2011; Schouten et al., 2012). Similar uncertainty is associated with the quantification of NO_3^- leaching due to its high dependence on site-specific conditions.

The use of experimental methods to quantify actual N losses to each environmental compartment and for different management practices is limited because routine application of such cost and labour-intensive methods is mostly not viable. Furthermore, experimental data are often not generalizable, due to inter-annual variability in weather patterns and management practices (Cameira et al., 2019b). Thus, one way to decrease the uncertainty associated with default values is the use of properly tested modelling tools (Bouraoui and Grizzetti, 2014). Physically based or process models include the relevant regulating factors to support the quantification of N transformations and transport and have proven their applicability for simulating NH_3 and N_2O emissions and NO_3^- leaching for different land use types (Butterbach-Bahl et al., 2013). Furthermore, integrated system modelling is considered an important tool for the application of a holistic approach, where the interactions among the different components of an agricultural system and the different environmental compartments are accounted (Kersebaum et al., 2015). The issue of pollution swapping, which until now has not received sufficient attention, can be addressed by modelling the effects of different options to select the most effective. Bouraoui and Grizzetti (2014) give a detailed presentation of several process models, pointing out their importance for the successful implementation of the WFD. Unfortunately, these models require large amounts of data, some of which can be difficult to find. Thus, model calibration and validation against experimental data is extremely important (Moore and Doherty, 2005; Kronvang et al., 2009; Kersebaum et al., 2015) and will improve the reliability of the N emission predictions (IPCC Tier III methodology, IPCC, 2006). On the other hand, gaseous emissions are measured only during the crop growing season despite the fact that such emissions might be highly relevant on a yearly basis (Hao, 2015; Chantigny et al., 2017; Adair et al., 2019). A successfully tested model can be used to predict time series of N fluxes for a sequence of several years, thus contributing to the estimation of the EFs for the various environmental compartments.

There are different possible setups to collect experimental data in order to calibrate and validate models. Drainage lysimeters are frequently used to monitor continuously NO_3^- leaching dynamics under controlled inputs of water and nutrients in long-term (>5 yr) studies. Goss et al. (2010) and Singh et al. (2018) discuss the use of different types of lysimeters and associated limitations. The use of lysimeters consists in a direct method since nitrate fluxes are measured. Indirect methods (e.g. soil cores and suction cups) measure nitrate concentrations, thus need to be multiplied by water fluxes derived from numerical models of the soil water balance to produce nitrate fluxes. There is not a unique single option to be preferred. Comparison of three different methods is presented Zotarelli et al. (2007).

In the present work, it was hypothesized that through modelling it is possible to overcome the constraints that arise when using individual experimental data in the quantification of N pollution swapping associated to slurry application practices. For this the N losses to soil, air, and water from a double cropping system receiving cattle slurry applied by injection and surface application within a Mediterranean region were assessed, using an integrated experimentation and modelling approach based on the Root Zone Water Quality Model (RZWQM2) (Ahuja et al., 2000). In particular, it was intended (i) to discuss the influence of different environmental factors on N losses and (ii) to contribute to the improvement of EFs estimation for Portugal and other countries with similar slurries, soils, crops, and climates.

2. Materials and methods

2.1. Experimental site

The present study was conducted at the Instituto Superior de Agronomia, University of Lisbon (38° 4″ N, 9° 10′ W, 62 m above sea level) in Portugal and it is part of a broader experiment conducted from 2012 to 2016. The climate is Mediterranean, characterized by hot and dry summers (30 years' daily average air temperature varies from 16 to 28 °C) and rainy and mild winters (30 years' daily average air temperature varies from 7 to 15 °C). Precipitation is concentrated between October and April, the long-term (1981–2010) average annual rainfall being 728.2 $\pm$ 183.3 mm. During the studied period the annual rainfall was 879.5 mm, 805.1 mm, 1042.7 mm, 380.5 mm, and 619.9 mm in 2012, 2013, 2014, 2015, and 2016, respectively, thus showing important inter-annual variability. On average, 88.4 $\pm$ 4.4% of the precipitation occurred from October to April. It is worth mentioning that the year 2015 was very dry and hot.

For the present work the experiments were conducted in 18 field drainage lysimeters, each containing 1 m^3 of soil (1 m × 1 m × 1 m). Lysimeters were filled with soil 19 years ago (2000). Nine of the lysimeters were filled with a sandy soil (SS, FAO Haplic Arenosol) collected in Pegões (Southern Portugal) and the other nine were filled with a sandy loam soil (SL, FAO Haplic Cambisol) from Castelo Branco (Central Portugal) (Table 1). The double cropping system used in the present study is the most commonly used in dairy farms from South Europe (Portugal, North of Spain, Italy, etc.). Thus, the lysimeters were cultivated with *Zea mays* cv. "Almagro" (maize) in spring-summer and *Avena strigosa* cv. "Saia" (oats) in autumn-winter, from 2012. Maize was seeded between May 10th and June 16th and had cycle duration of 111 $\pm$ 6 days. Oats was seeded between November 12th and December 4th and its average cycle duration was 139 $\pm$ 20 days. Crop density was around 70,000 and 250,000 plants h^{-1} for maize and oats, respectively. For each soil, three lysimeters acted as a control (no fertilization) and six others were amended one week before seeding, with an amount of dairy cattle slurry close to 2200 and 5200 kg ha^{-1} for oats and maize, respectively (90 and 170 kg N ha^{-1} or 30 and 70 kg NH_4^+-N ha^{-1}). In three of these lysimeters, slurry was injected while in the other three it was band-applied on the soil surface. The latter is a practice used extensively in Southern Europe, while the incorporation or injection of liquid effluents is compulsory for farmers in the Vulnerable Zones to Nitrates. More details about the slurry composition and application can be found in Fangueiro et al. (2018).

As the crops were intended for animal feed, no stover/straw was left on the field. However, an estimated amount of 1000 kg ha^{-1} of 10-cm stalks was left in the field after harvest, with C/N ratios of 79 and 55 for maize and oats, respectively.

The oats cycle develops during the autumn-winter rainy season, so the crop was rain fed. Maize cycle coincides with the spring-summer hot and dry season typical of the Mediterranean climates, so the crop was irrigated with a drip system, using water from the public water network. Each soil type was served by an independent irrigation sector consisting of two drip lines (UniRam™ by Netafim) with an internal diameter of 13.8 mm, one per crop row, and with a length of 20 m. The pressure compensating emitters (iDrop PC, Irritec), with an average discharge of 4 L h^{-1}, were spaced 0.20 m apart. Irrigation was applied daily, the amounts being adjusted, independently for each soil, on a weekly basis using the soil water balance and the crop coefficient method (Allen et al., 1998).

2.2. Measurements

Plant heights and rooting depths were measured, in randomly selected plants, in significant crop stages for the crop empirical model parameterization, within the RZWQM2. Meteorological data from 2012 to 2016 were collected in a nearby meteorological station (38° 42′ N, 9° 10′ W).

Water content reflectometers, previously calibrated for each soil (CS616 and CS625, Campbell Scientific, Inc.), were installed at a depth of 20 cm to monitor the soil water content (SWC) from November 2014. The reason for choosing this shallow depth is that it was intended to calculate the water filled pore space (WFPS) and relate it conceptually to the measured N_2O emissions. The soil temperature was monitored in one lysimeter of each soil, using temperature probes (Campbell Scientific) also installed at 20 cm. All probes were connected to a data logger (CR10, Campbell Scientific LTD) which recorded average values every 30 min. The soil-atmosphere exchange of N_2O was quantified from 2012 to 2015 using the closed chamber technique. Ammonia (NH_3) measurements were taken using the dynamic chamber technique, for almost 72 h after soil amendment. A detailed description of the gas measurements can be found in Harrison et al. (1995) and Fangueiro et al. (2015, 2017). Drainage water from the lysimeters was collected from 2014, in the access tunnel directly beneath them. The measurement frequency depended on the climatic conditions in the previous days, particularly if there was enough precipitation or irrigation to produce drainage water to collect. The amount of collected leachates was quantified using the volumetric method, after which subsamples were taken for nitrate nitrogen (NO_3^--N) analysis by molecular absorption spectroscopy in a segmented-flow system (San Plus, Slakar, Breda, the Netherlands), using the Griess-Ilosvay reagent (Houba et al., 1989).

Table 1
Selected properties of the soils used in the experiment (adapted from Cameira et al., 2019b).

Soil type	Depth	Particle size distribution (%)				BD	$\theta_{v\ (cm3\ cm-3)}$		Ks	pH	OM
	cm	Coarse sand	Fine sand	Silt	Clay	g cm^{-3}	33 kPa	1500 kPa	cm h^{-1}	(%)	(%)
Sandy	0–50	70.7	17.0	9.7	2.6	1.48	0.108	0.020	21.0	7.3	0.8
	50–100	69.0	18.0	10.4	2.6	1.41	0.108	0.021	–	–	–
Sandy loam	0–50	19.2	55.8	15.0	10.0	1.44	0.263	0.057	2.6	6.6	1.5
	50–100	20.1	55.8	14.1	10.0	1.48	0.263	0.056	–	–	–

BD is bulk density, θ_v is the volumetric water content, at 33 and 1500 kPa representing field capacity (θ_{FC}) and wilting point (θ_{WP}) respectively, Ks is the saturated hydraulic conductivity, pH is the potential of hydrogen and OM is the soil organic matter.

2.3. Modelling

2.3.1. RZWQM2 model overview

The Root Zone Water Quality Model 2 (RZWQM2) was the process model chosen for this study because: a) it simulates the interactions between plant, soil, hydrologic, management (irrigation, fertilization, and tillage), and atmospheric factors; b) it has been successfully used before in Mediterranean agro-ecosystems (Cameira et al., 2005, 2014a, 2014b, 2019b); and c) it was recently modified to simulate N_2O emissions. Nevertheless, previous works with modified RZWQM2 refer only to synthetic fertilizers. Also, none of the applications tested the model against N data in the different environmental compartments measured simultaneously (N_2O emissions to the atmosphere, ammonia volatilization, and nitrate leaching to the groundwater).

RZWQM2 is a comprehensive, process based agro-ecosystem model that simulates the complexity of the main drivers affecting the N cycle in the soil-plant system and the impacts of management upon the different environmental compartments (Ahuja et al., 2000). The processes and equations in RZWQM2 have been extensively described in previous publications, with specific applications: for example, soil water fluxes and retention (Cameira et al., 2005), crop uptake (Malone et al., 2007), NO_3^- leaching (Fang et al., 2012; Cameira et al., 2014a, 2014b), and N_2O emissions (Fang et al., 2015; Wang et al., 2016; Gillette et al., 2017).

The soil water module uses the Green-Ampt equation for infiltration during irrigation or rainfall events and Richards' equation for water redistribution between events. Potential evapotranspiration is based on the Shuttleworth and Wallace dual surface version of the Penman-Monteith equation. Plant water uptake is simulated with the Nimah-Hanks equation and coupled to Richards' equation as a sink term. At present the RZWQM2 uses a simplified empirical model for oats, to compute daily uptake of water and N from the soil. The total biomass growth and total N uptake during the season are assumed to be known, and the progress of shoot and root growth with time is represented by linear segments. The organic matter (OM) and N component simulates the major pathways of the soil C/N dynamics, including mineralization–immobilization, ammonia volatilization, and nitrification. The OM is distributed over five computational pools and is decomposed by three microbial mass populations. First-order decomposition rates for each organic C pool are assumed, with rate coefficients as functions of soil temperature, soil oxygen concentration, soil C substrate amount, soil pH, and soil moisture. The two sources of N_2O are nitrification and denitrification, which are calculated with zero-order and first-order kinetics, respectively, the water-filled pore space playing a significant role. A detailed formulation is presented in Fang et al. (2015).

2.3.2. Parameterization and sensitivity analysis

The model was parameterized using measured, estimated, and literature-based data. For the hydrologic component, measured basic soil physical properties influencing soil water retention and fluxes were used: for example, soil texture, bulk density (BD), volumetric moisture (θ_v) at 33 and 1500 kPa, and saturated hydraulic conductivity (K_{sat}). The parameters of the Brooks and Corey soil water retention curve - $\theta(h)$ and the conductivity/suction relationship, $K(h)$ - were estimated using the methodology described in Cameira et al. (2014a).

The RZWQM2 sub-model Quick Plant is an empirical plant module developed to simulate the presence of a sink for water and nitrate for the crops, such as the ones studied in the present work, and for which there is no deterministic model. Thus, as oats and silage maize yields are not being modelled, a simple parametrization is required regarding maximum crop height (1.5 and 0.6 m for maize and oats respectively), maximum depth of roots (1.0 and 0.8 m), LAI (5 and 3.7 $m^2\ m^{-2}$), and maximum N uptake (52.9 and 26.9 kg ha^{-1}).

The processes related to C and N were parameterized based upon the measured OM content of the soils. For the organic pools partitioning, the initial soil organic C pools were set based on the OM at each soil depth, using the wizard provided in RZWQM2. Then, the model was run for a period of 10 years under the current management practices in order to equilibrate the humus and microorganisms pools (Ma et al., 2011). Few studies have reported the use of the RZWQM2 model to simulate N_2O emissions. Thus, a local model analysis was performed to determine which input parameters caused the largest variation in N_2O emissions and if there was any parameter whose variability had a negligible effect. The outputs were obtained by varying the parameters $\pm30\%$ around a reference value used for model parameterization (baseline). Each value was manually changed while the others were kept unchanged (Norton, 2015). Based upon past work and experience, relevant model parameters were selected as key for the process (Table SM1 in Supplementary material).

2.3.3. Calibration and validation

Based upon the sensitivity analysis results, the model was calibrated following an iterative trial-and-error adjustment procedure during the spring maize - winter oats crop seasons 2014–2015 and 2015–2016, and validated using independent data from the 2012–2013, 2013–2104, and 2016–2017 seasons. The procedure was controlled by the measured values of soil water content and temperature at the depth of 20 cm, drainage and NO_3^- leaching at the depth of 100 cm, and N_2O and NH_3 emissions to the atmosphere. The latter (NH_3 measurements) were available only for the winter oats seasons. The soil water dynamics component of the model was calibrated first, followed by the OM and soil N component. Finally, the N_2O emissions module was adjusted. The process was iterated several times in order to minimize the error propagation between components/modules.

In addition to the graphical analysis, the accuracy of model predictions was evaluated by the root mean squared error (RMSE), the Nash–Sutcliffe modelling efficiency (NSME) (Nash and Sutcliffe, 1970), and the coefficient of determination (r^2). For soil water and N predictions the expected minimum values for NSME and r^2 are 0.7 and 0.8, respectively (Ma et al., 2011). In addition, for soil water the RMSE is expected to be lower than the mean standard deviation of the measurements (MSD) (Cameira et al., 2005). Maximum absolute error (MAE) was also used to indicate the maximum deviations between simulations and measurements in the N related data series.

3. Results and discussion

3.1. Model sensitivity analysis

For the studied systems, the parameters that most influence the N_2O emissions fall into the soil properties group and N_2O rate coefficients group (Fig. SM1). The model outputs showed low sensitivity to the initial conditions of soil water and temperature. The simulated N_2O fluxes were more sensitive to input variations for the sandy soil system, which is probably related to the stronger kinetics of the water related processes that highly influence both N transport and transformations. Thus, the parameters chosen for the calibration process were the soil water content at field capacity (θ_{FC}), the saturated hydraulic conductivity (K_{sat}), the fractionation of OM among the different decomposition pools and the respective inter-pool coefficients, the rate of nitrification (R_{NIT}), and the contribution of nitrification to N_2O production (f_{NIT_N2O}).

3.2. Model calibration and validation

3.2.1. Soil water and N related parameters

Calibration of the soil hydraulic parameters was particularly important for the sandy soil, significant changes relative to the initial values being observed (Table SM2 in Supplementary material). In fact, for this soil, the calibrated K_{sat} and θ_{FC}, that highly influence the water fluxes in the soil, varied between 27.5 and 21.5%, on average, respectively.

As a rule of thumb, the expected annual N mineralization for the top 30 cm of soil is around 20 kg N ha^{-1} $year^{-1}$ per 1% of endogenous OM (Scheppers and Mosier, 1991). For the crop growing periods, values of 24 and 45 kg ha^{-1} per year are expected for the top 60 cm of the sandy and sandy loam soil, respectively. To meet these values: i) the initial distribution of the soil OM among the decomposition pools was set to 4% in the fast humus, 16% in the intermediate humus, and 80% in the slowly decomposing humus pools; and ii) more C was allocated in time to the quickly decomposing pools by changing the inter-pool transfer coefficients (Fig. 1). For both soils it was necessary to allocate more C to the intermediate pools, so the coefficients C1 (slow residue to intermediate humus) and C2 (fast residue to fast humus) were increased (Table 2). For the sandy loam soil, it was necessary to decrease the C3 and C4 coefficients, to further increase C in the fast and intermediate pools. By decreasing the transfer coefficient between the fast and intermediate decomposition pools, short-term mineralization increases since the amount of OM in the fast pool increases. On the other hand, when the transfer coefficient between the intermediate and slow pools decreases, short/medium-term mineralization will increase as part of the slow decomposing OM is reallocated to the intermediate pool.

3.2.2. Soil water, drainage, and soil temperature predictions

Values of soil water content (SWC) and soil temperature (T) at 20 cm depth as well as values of drainage (D) at 100 cm depth, measured in field conditions and simulated with the RZWQM2 model, are presented in Figs. 2 and 3 for the sandy soil and the sandy loam soil, respectively. The variations in soil moisture due to precipitation, irrigation, and crop uptake were adequately simulated, which is the basis for good predictions of the N dynamics. Furthermore, the differences between soils with respect to water retention and permeability were captured by the model. Indeed, the sandy soil (Fig. 2) had a lower SWC than the sandy loam soil, with a more immediate response to precipitation inputs. RZWQM2 simulated well the daily drainage fluxes during the oats and maize growing seasons, under both precipitation and drip irrigation. Not only was the drainage peak on 22/11/2014 well predicted, but also the lower values in the remaining measurement days. The predictions of soil temperature were less accurate than for SWC and D, but still considered reasonably good since the model reproduced the seasonal patterns. The periods of higher water dynamics in the soil are

Table 2
N related parameters values obtained after calibration.

Soil	Interpool coefficients (dim)				Reaction rates (dim)	
	C1	C2	C3	C4	R_{NIT}	$N_2O\_f_{NIT}$
Sandy	0.3	0.6	0.6	0.7	1.5×10^{-9}	0.0016
Sandy loam	0.3	0.6	0.3	0.3	1×10^{-9}	0.0012
Default	0.1	0.1	0.6	0.4	1×10^{-9}	0.0016

C_1 is the slow residue to intermediate humus pool, C_2 is the fast residue to fast humus pool, C_3 is the fast to intermediate humus pool, C_4 is the intermediate to slow pool, R_{NIT} is the nitrification coefficient, and $N_2O\_f_{NIT}$ is amount of N_2O produced by nitrification (dim = dimensionless).

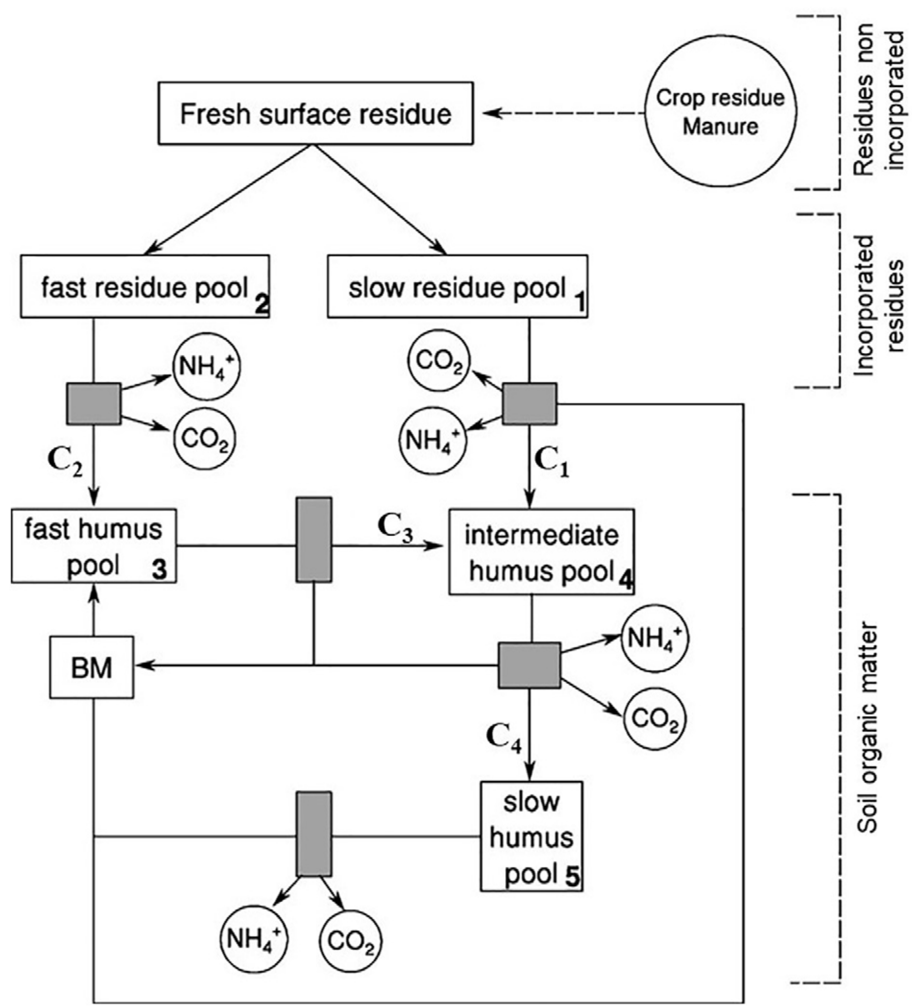

Fig. 1. A schematic diagram of residue and soil organic matter pools in RZWQM2. C1, C2, C3, and C4 are inter-pool mass transfer coefficients; BM is microbial biomass (adapted from Cameira et al., 2007).

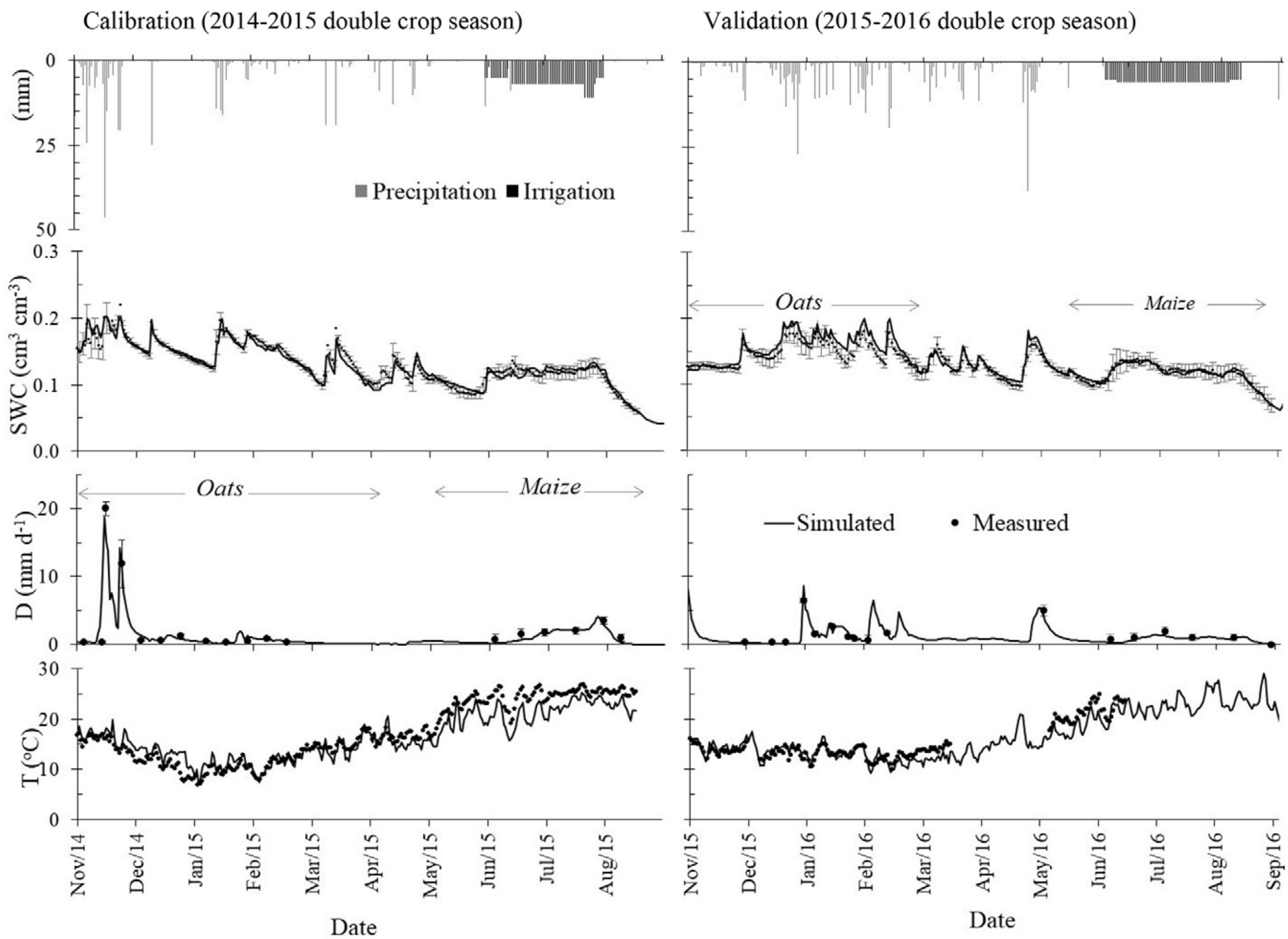

Fig. 2. Simulated and measured values of soil water content (SWC, average with standard deviation) at 20 cm, drainage (D, average with standard deviation) at 100 cm, and soil temperature (T) at 20 cm, for the sandy soil.

the ones with lower adherence to the measured data. These periods correspond to the beginning of the oats cycle, when the precipitation was more intense, and the irrigation period of the maize cycle. Furthermore, while the higher temperatures were overestimated the lower temperatures were underestimated. A possible explanation is that the RZWQM2 heat module uses air temperature as the boundary condition at the soil surface (Fang et al., 2015). Nevertheless, during the summer season the temperature of the air inside the maize canopy is much higher than in the atmosphere above, where the air temperature is measured.

The RMSE of the soil water predictions was always lower than the average standard deviation of the measured values (MSD) (Table 3). Both the NSME and the r^2 met the minimum requirement for soil water content and drainage (0.7 and 0.8, respectively). The statistics had lower values for the soil temperature predictions. Overall, RZWQM2 reasonably simulated soil temperature, with RMSEs ranging from 3.48 to 3.32 °C and r^2 around 0.65, similar to those reported in other work (e.g. Fang et al., 2015; Gillette et al., 2017, 2018).

3.2.3. N fluxes to soil, air, and water

The NH_3 emissions measured in both soils after slurry injection were residual (see Fangueiro et al., 2018). Hence, the NH_3 emissions (measured and simulated values) presented refer to band applied slurry. Due to the daily time step outputs of the model, it was not possible to simulate the NH_3 fluxes and compare them to measurements presented in Fig. 4. Thus, only cumulative NH_3 emissions were used for calibration (Table 4). Table 4 shows that the model captured not only the differences between soil types but also the inter-annual variability associated with different precipitation regimes, when simulating cumulative NH_3 emissions. Nevertheless, the correlation between measured and simulated values was more significant in SS soil relative to SLS soil.

Figs. 5 and 6 show simulated versus measured values of NO_3^--N leaching at 100 cm and N_2O emissions at the soil surface, for the calibration (2013/2014) and the validation (2014/2015) double crop seasons. The second validation period is presented as Supplementary material (Fig. SM2). Precipitation, irrigation, and water filled pore space (WFPS) are also presented to allow an integrated conceptual interpretation. There was an overall agreement between the simulations and measurements concerning N flux dynamics, the simulated fluxes having the same order of magnitude as the measured ones, and a coincidence in the peaks and in the temporal distributions. The model was able to capture the differences between the soils (the timing and the magnitude of the N_2O emissions and NO_3^--N leaching differed) and also the inter-annual variability associated with the climate, in particular the precipitation. Therefore, higher NO_3^- leaching was predicted for the 2012–2013 period (Fig. SM2), while for the 2014–2015 season higher N_2O emissions were predicted (Figs. 5 and 6). Regarding the statistical indicators (Table 5), the NSME values are similar to the ones found in the literature (Ma et al., 2011) and expected for N-related simulations. The MAE can bias the evaluation of model accuracy, so that high values might be associated with a one-day delay or an advance in the simulated peaks (e.g. in the SLS in May 2013, the simulated peak occurs one day after the measured). Nevertheless, an over/underestimation of the peak can also affect the MAE value (e.g. SS, April 2014; SLS, November 2014). The corresponding values of r^2 show that the model explained reasonably well the variability of the response data around its mean and met the requirements for N-related simulations (Ma et al., 2011). Gillette

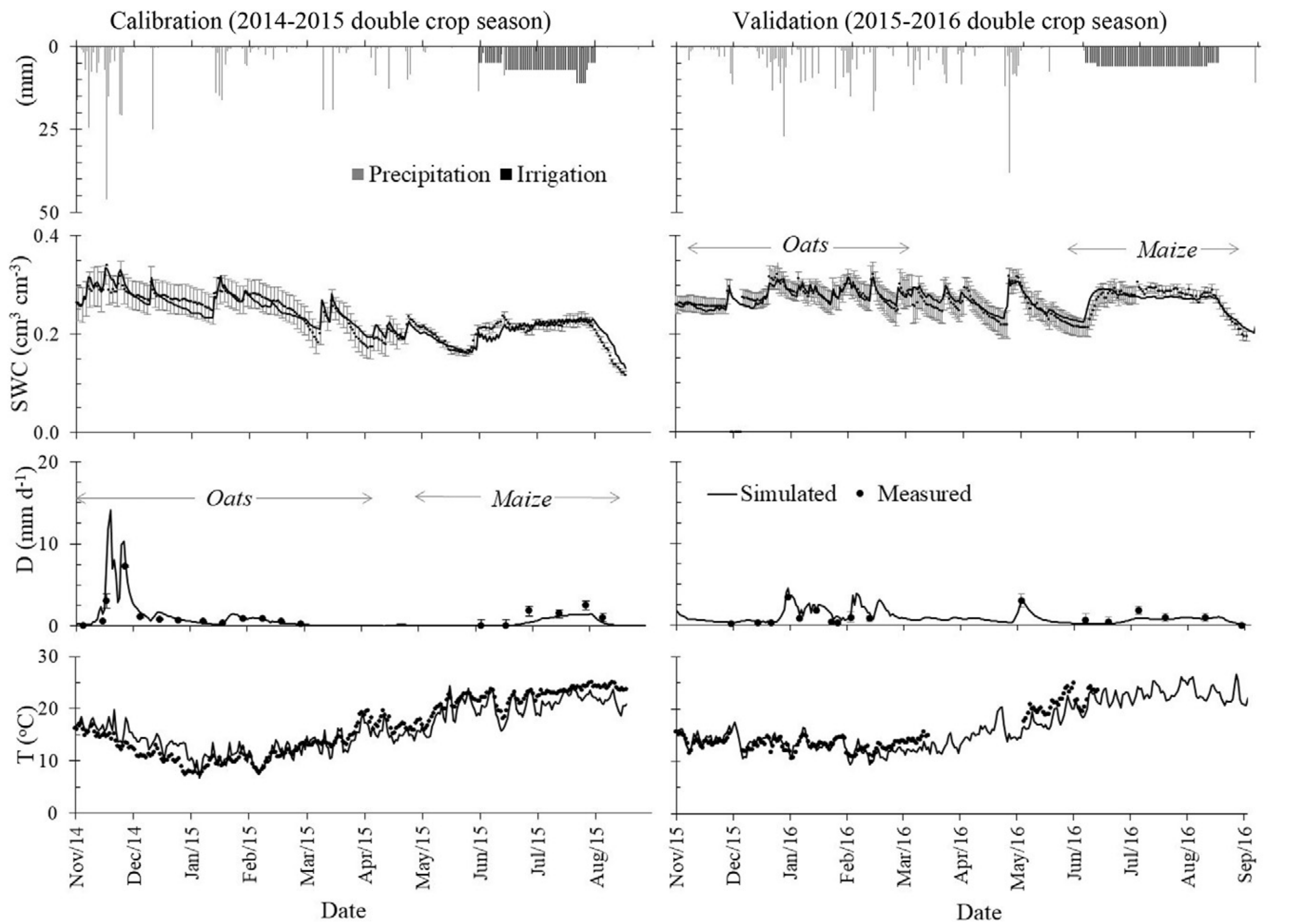

Fig. 3. Simulated and measured values of soil water content (SWC, average with standard deviation) at 20 cm, drainage (D, average with standard deviation) at 100 cm, and soil temperature (T) at 20 cm, for the sandy loam soil.

et al. (2017) tested the ability of the modified RZWQM2 model to predict the effect of tillage and N fertilization amount on N_2O emissions in an irrigated corn field in Colorado: it underestimated N_2O emissions, by 1.5% and 7.1%, respectively, under no-tillage and conventional tillage. Overall, similar results were obtained by other authors in comparable studies (Fang et al., 2012; Wagena et al., 2017).

The RZWQM2 allowed us not only to simulate N_2O emissions during the measurement period, when emissions are generally more significant, but also to estimate N_2O emissions during the non-growing period. Indeed, some significant peaks of N_2O emissions were observed in the simulation performed for the 2013–2014 growing season (Fig. 5), in both soils, between September and November. Similarly, some peaks were simulated in the SLS during the 2014–2015 growing season (Fig. 6).

Table 3
Model accuracy statistics for soil water and temperature, and drainage.

Indicator	Sandy soil			Sandy loam soil		
	SWC (cm^3 cm^{-3})	D (mm)	T (°C)	SWC (cm^3 cm^{-3})	D (mm)	T (°C)
Calibration						
# samples	286	19	250	286	18	250
MSD	0.006	0.513	–	0.013	0.133	–
RMSE	0.004	1.290	3.480	0.005	0.663	3.320
NSME (%)	95	94	57	95	88	51
r^2 (dim)	0.93	0.93	0.65	0.93	0.87	0.67
Validation						
# samples	294	17	113	294	17	113
MSD	0.015	0.101	–	0.018	0.018	–
RMSE	0.009	0.689	1.035	0.012	0.510	1.048
NSME (%)	82	88	26	78	79	28
r^2 (dim)	0.92	0.90	0.63	0.78	0.79	0.63

SWC = soil water content, D = drainage, T = soil temperature, MSD = mean standard deviation, RMSE = root mean squared error, NSME = model efficiency (%) and r^2 = determination coefficient (dim.).

3.3. Impact of environmental conditions on N dynamics

The N dynamics in soils amended with cattle slurry are strongly affected by environmental conditions such as soil characteristics, temperature, and/or water balance. In the present study, no significant differences were observed between the temporal series of temperature

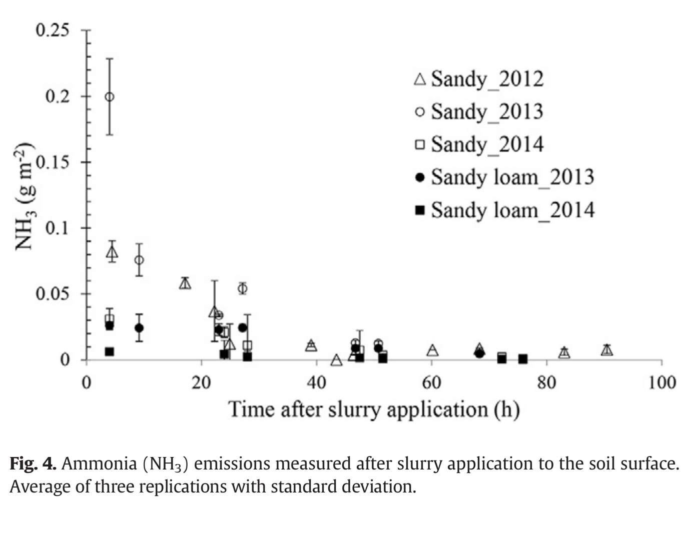

Fig. 4. Ammonia (NH_3) emissions measured after slurry application to the soil surface. Average of three replications with standard deviation.

Table 4
Simulated and measured cumulative ammonia volatilization (NH_4^+-N, g m^{-2}) after slurry application to the soil surface during winter oats seasons, average of three years with standard deviation (SD).

year	Period of measurement (h)	Sandy soil		
		Measured		Simulated
		Average	SD	
2012	90.5	1.89	0.15	1.97
2013	75.9	2.51	0.18	2.10
2014	68.3	0.86	0.08	0.90
Year	Period of measurement (h)	Sandy loam soil		
		Measured		Simulated
		Average	SD	
2012	90.5	[a]	–	1.26
2013	75.9	1.03	0.12	1.33
2014	68.3	0.19	0.02	0.38

[a] Not available.

measured for the sandy soil and that of the sandy loam soil (data not shown). Ammonia emissions are quite sensitive to soil characteristics, since NH_4^+ can be fixed on clays. Some differences were observed between the two soils (Table 4), with a probable direct impact on NO_3^- and N_2O fluxes. Such differences might be due to the lower gas diffusion in the SLS as well as potential NH_4^+ fixation on clay. Indeed, in theory, the lower the NH_3 emissions, the greater the available NH_4^+ that can be nitrified and potentially leached or lost as N_2O (Sommer et al., 2003). The results presented here support this concept, as shown later.

Nitrate leaching relies mainly on NO_3^- availability in the soil, water drainage, and the interaction of both parameters. The sandy soil is very permeable, showing a low to medium-low SWC (0.10 to 0.20 cm^3 cm^{-3}), often with sharp variations due to irrigation and precipitation (Fig. 2). During the precipitation days, the SWC at 25 cm depth rises abruptly above field capacity, indicating drainage to the underlying soil layers. In fact, in the 10–30 days after slurry application drainage was significant, creating favorable conditions for potential NO_3^- leaching. The NO_3^- flux (Figs. 5 and 6) follows the tendency of drainage (D), showing the importance of convection as a solute transport process. In the sandy loam soil the SWC at 25 cm depth is often below field capacity (Fig. 3), leading to less drainage than in the sandy soil. However, the drainage flux has peaks that are 30% lower in the sandy soil compared to the SLS soil (Fig. 3). Nevertheless, the potential for NO_3^- leaching was higher in the sandy soil, such that drainage occurred mainly between 10 and 40 days after slurry application, when a significant part of the applied NH_4^+ (not lost as NH_3) was already nitrified. Nitrous oxide is produced in soil by the denitrification and nitrification processes, which are controlled by a complex set of parameters including several soil characteristics such as the availability of oxygen and NO_3^- (Bouwman, 1990, 1996; Butterbach-Bahl et al., 2013). For these reasons, very different values of N_2O emissions exist in the literature, a result of the environmental and management conditions. Rabot et al. (2014) found that for WFPS < 0.62 there is low N_2O production, whereas for WFPS higher than 0.95 the diffusion of the gas in the soil is low. They found that the WFPS values that contributed most to the production of N_2O were between 0.6 and 0.79, due to an increase in the gradient between the surface and the atmosphere. There is entrapment of N_2O during wet periods - which originates peaks during dry periods, from the release of N_2O. A high C content can also increase denitrification and can produce an increase in N_2O or a reduction in N_2O/N_2 (Signor and Cerri, 2013).

In the present study, the N_2O emissions occurred until approximately one month after the slurry applications, showing values of low/medium magnitude and varying between 0 and 20 g ha^{-1}. In the sandy soil, the WFPS was always below 60% (Figs. 5 and 6), creating conditions unfavorable for the denitrification process (Dobbie and Smith, 2001); this suggests that most of the N_2O is a “by-product” from the nitrification process.

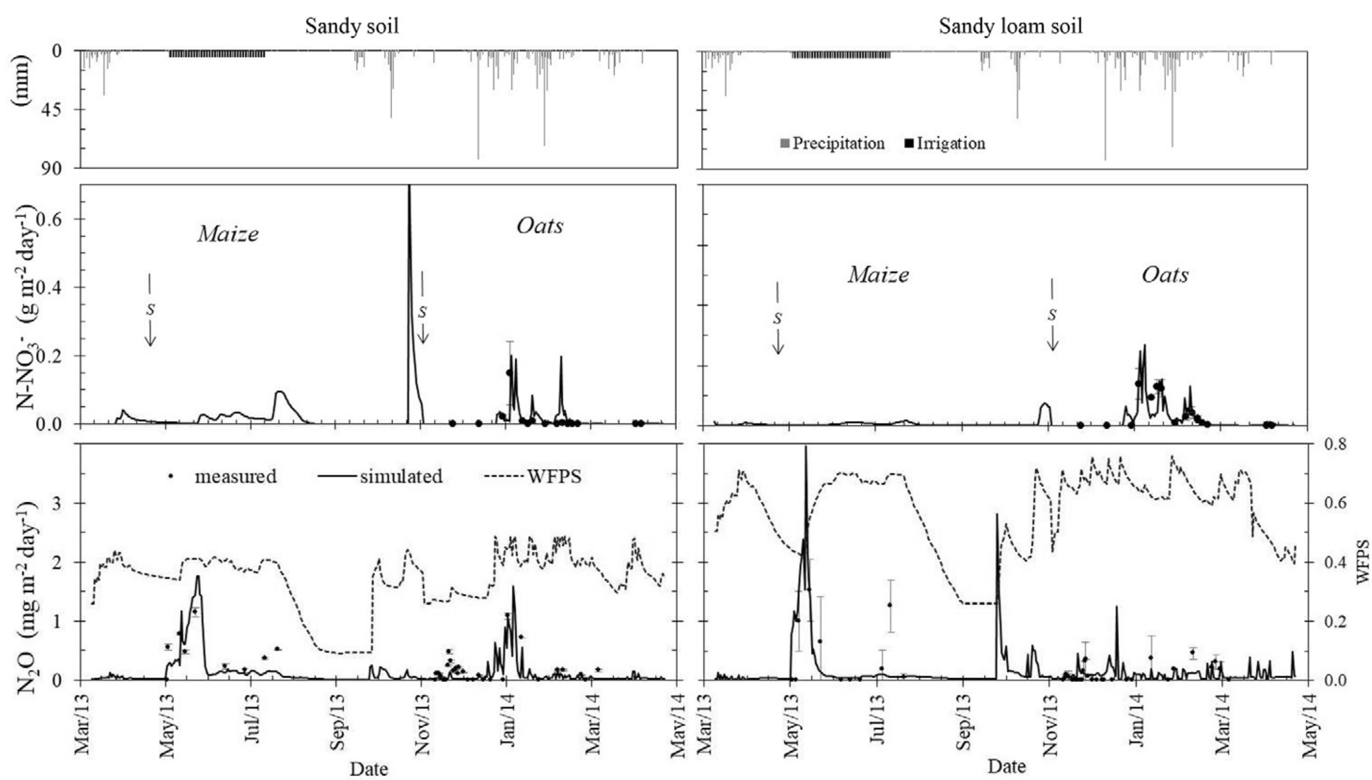

Fig. 5. Simulated versus measured values of nitrate (N-NO_3^-) leaching at the depth of 100 cm (average with standard deviation) and of N_2O emissions (average with standard deviation) for the calibration double crop season 2013/2014 (*S* indicates the slurry application day, WFPS is the water filled pore space).

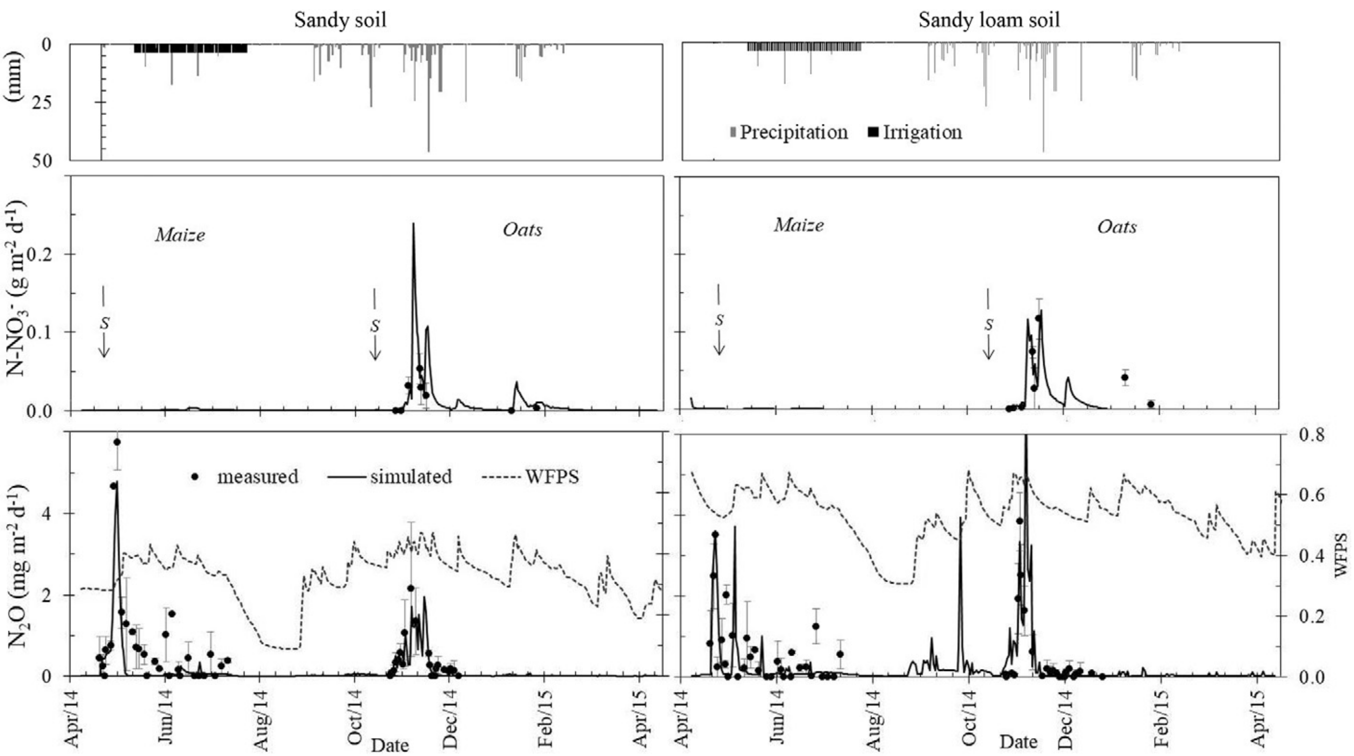

Fig. 6. Simulated versus measured values of nitrate (N-NO_3^-) leaching at the depth of 100 cm (average with standard deviation) and of N_2O emissions (average with standard deviation) for the validation double crop season 2014/2015 (*S* indicates the slurry application day, WFPS is the water filled pore space).

In the sandy loam soil, the N_2O flux started after slurry application and stopped a few days sooner than in the sandy soil, varying between 0 and 75 g N ha^{-1}. The period of greater N_2O emissions (0 to 25 days after slurry application) coincided with the period when WFPS was above 60%, indicating a larger contribution of the denitrification process than in the sandy soil (Dobbie and Smith, 2001). Due to its lower water conductivity, the sandy loam soil becomes anaerobic more easily and such conditions persisted for longer than in the coarser textured soil, leading to high N_2O emissions. It is generally considered that finer textured soils provide conditions more favorable for denitrification and N_2O emission at lower soil moisture than coarser soils, which favor nitrification (Parton et al., 1996; Bollmann and Conrad, 1998).

For both soils, there were two or more peaks after slurry application, the first resulting from the nitrification of the NH_4^+ applied in the slurry and the second produced by the denitrification of the resulting NO_3^--N when the conditions were favorable; that is, when the WFPS was higher than 60% (Zaman et al., 2009; Rabot et al., 2014). In agricultural soils the largest proportion of N_2O emissions is attributed to the large pulses that occur after irrigation and precipitation events, which stimulate denitrifying microorganisms (Barton et al., 2013; Trost et al., 2013).

Fig. 7 shows the major water balance components for both soils (average of four years). For both soils, evapotranspiration (ETa) was the most significant "loss" during the maize cycle; it was predominantly satisfied by irrigation although the crop also used water stored in the soil (VS). During the oats growing period (winter) precipitation was the main input and drainage (D) the most significant output. In the present study, drainage was mainly associated with precipitation, underlining that irrigation was properly scheduled. However, in situations where irrigation is used in excess, drainage (and potential NO_3^- leaching) might be more significant in summer crops than in winter crops. When looking at the whole double crop season, the crop water use in the sandy loam soil exceeded drainage while in the sandy soil

Table 5
Model accuracy statistics for nitrate leaching and N_2O emission fluxes after model calibration.

Indicator	Calibration (one season)				Validation (2 seasons)			
	Sandy soil		Sandy loam soil		Sandy soil		Sandy loam soil	
	φNO_3^- (g m^{-2} d^{-1})	φN_2O (mg m^{-2} d^{-1})	φNO_3^- (g m^{-2} d^{-1})	φN_2O (mg m^{-2} d^{-1})	φNO_3^- (g m^{-2} d^{-1})	φN_2O (mg m^{-2} d^{-1})	φNO_3^- (g m^{-2} d^{-1})	φN_2O (mg m^{-2} d^{-1})
# samples	15	40	15	43	23	90	23	93
$\overline{O}$	0.013	0.226	0.040	0.188	0.018	0.435	0.034	0.519
$\overline{S}$	0.024	0.167	0.035	0.195	0.044	0.317	0.023	0.512
RMSE	0.019	0.153	0.029	0.15	0.026	0.356	0.026	0.472
NSME (%)	72	65	69	70	61	64	67	74
MAE	0.06	0.412	0.187	1.09	0.534	1.4	0.064	1.96
R^2	0.89	0.80	0.7	0.77	0.68	0.73	0.81	0.76

φNO_3^- = nitrate leaching flux, φN_2O = nitrous oxide emission, $\overline{O}$ = measured mean, MSD = mean standard deviation, $\overline{S}$ = simulated mean, RMSE = root mean squared error, NSME = model efficiency (%), MAE = maximum absolute error, and R^2 = determination coefficient (dim.).

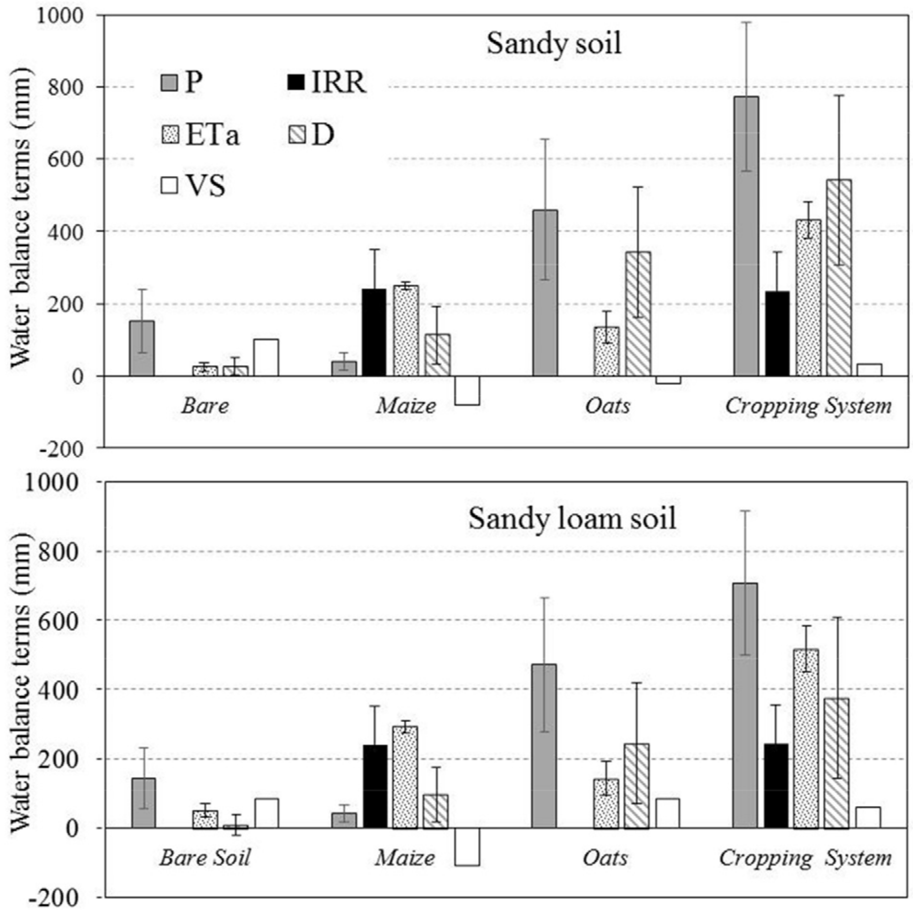

Fig. 7. Major water balance terms, average of four years with standard deviation. Top graph – sandy soil; bottom graph – sandy loam soil (P – precipitation, ETa – actual evapotranspiration, VS – variation in storage, IRR – irrigation, D- drainage).

the opposite situation was observed, with a direct impact on the N budget for both soils.

3.4. N balances for slurry band application vs slurry injection

Once the model had been calibrated and validated for years with considerable inter-annual precipitation differences, it was used to predict N-related processes whose measurement in the field requires a lot of labour and time and is of high cost. The N budget (NB) was predicted for two slurry application methods, surface band application and injection. Fig. 8 shows the main components of the NB for the full double crop system and for the different components: bare soil period, spring-summer irrigated crop (silage maize) period, and autumn-winter rain-fed crop (oats) period. Some N balance components were not included in this study since they were null, which was the case of nitrates in irrigation water, or residual, which was the case of atmospheric N deposition and biological N fixation. Experimental data regarding changes in the N soil storage was not available, so this term is also missing, which can add some uncertainty to the N balance modelling results. For the surface application method, the overall results show that the mineralization (including endogenous OM and crop residues) was higher for the sandy loam soil, probably due to its higher C content. Regarding outputs, N uptake was higher for the sandy loam soil since N leaching was lower, in particular during the oats season. For both soils, gas losses were higher during the maize crop season while leaching was higher for the oats season. The main differences when comparing surface application and slurry injection are that for the latter the gas losses were somewhat smaller, mainly due to the reduction in NH_3 volatilization. At the same time, as more nitrate was available in the soil, leaching losses were higher than with surface application. While with surface application, volatilization was the main path for N loss, when the slurry was injected leaching was the main loss process, particularly during the oats season (Fig. SM3). Despite their lower values, N_2O emissions are of great importance due to the strong greenhouse gas effect of this gas. Nitrous oxide emissions were higher in the sandy loam soil when the slurry was injected, compared to the surface application. During the bare soil periods, the highest losses occurred as N_2O in the sandy loam soil and by leaching in the sandy soil. Similarly, Jamali et al. (2016) found N_2O emissions from fallow soils to be 6.2 and 2.4 times higher than from cultivated soils.

3.5. Emission and leaching factors, water inputs, and slurry application method

The daily N flux series for the full double crop system allowed the estimation of N_2O emission factors and NO_3^- leaching factors. Fig. 9 shows the average emission [EF = (N_2O emission-N_2O background)/N applied] and leaching factors [LF = (NO_3^- leaching − background NO_3^- leaching)/N applied] calculated for both soils, when the cattle slurry was applied at the surface without incorporation and when it was injected. The background N_2O and NO_3^- fluxes result only from the turnover of soil organic N and were calculated for both soils using the previously calibrated model without any external N inputs. The calculated EFs varied from 0.39% to 0.94% for cattle slurry injection and from 0.20% to 0.40% for band application in the sandy soil. For the sandy loam soil, injection yielded EFs from 0.62% to 1.40% against 0.24% to 0.89% with band application. The average LF values were higher for the sandy soil with slurry injection: the values varied from 0.04 to

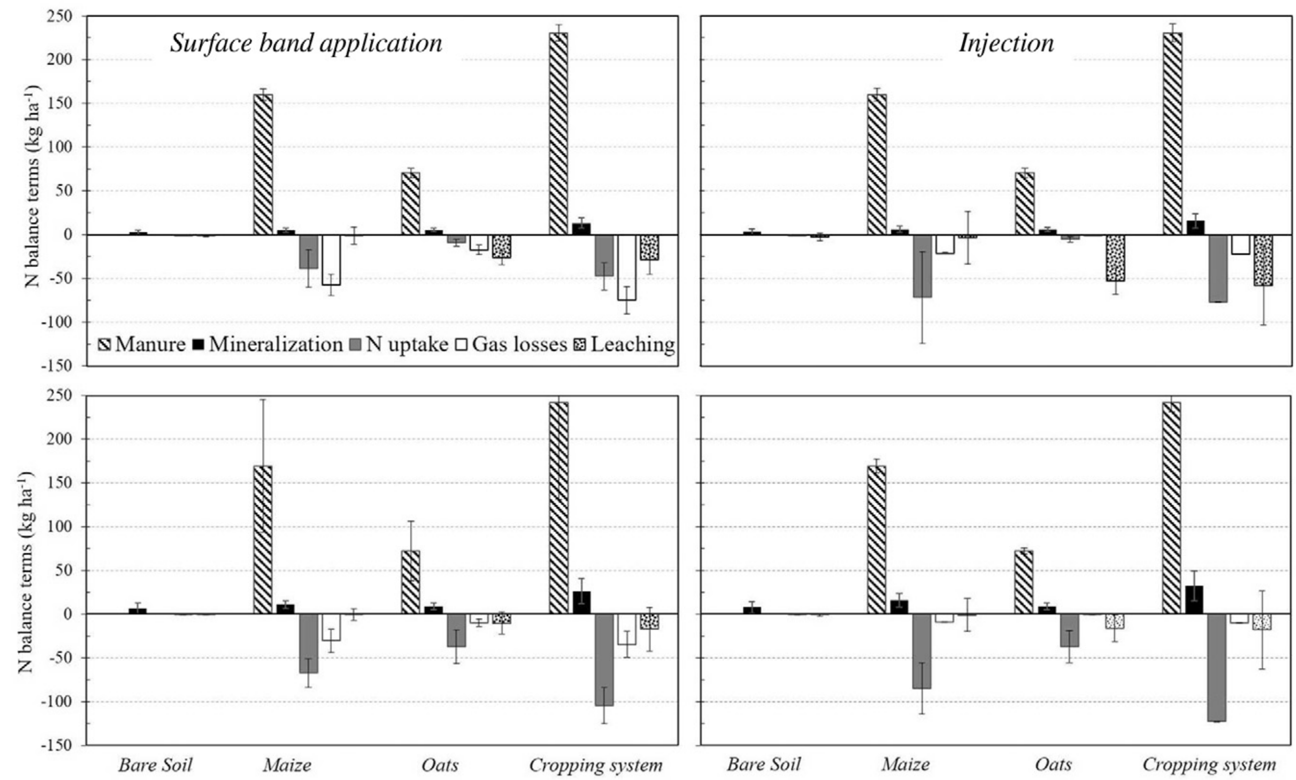

Fig. 8. Major N balance terms, average of four years with standard deviation. Top graphs – sandy soil; bottom graphs – sandy loam soil (P – precipitation, ETa – actual evapotranspiration, VS – variation in storage, IRR – irrigation, D- drainage).

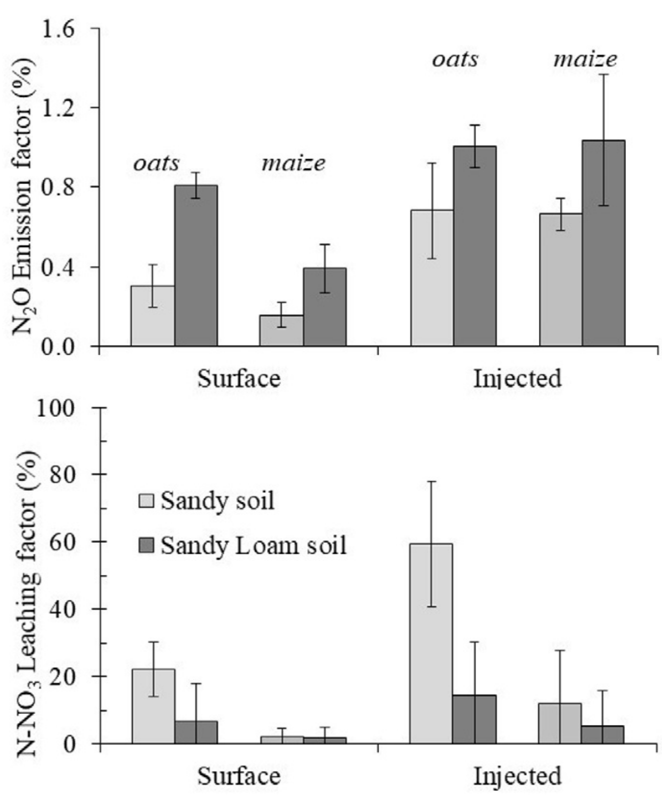

Fig. 9. Emission factors for winter oats fertilized with dairy slurry and cultivated in the sandy soil (SS) and the sandy loam soil (SLS) during the four years in which the experimental data were obtained. Leaching factors for the four studied double crop seasons, averages with standard deviations.

82.5 for injection and from 0.0 to 31.8 for band application. For the sandy loam soil injection yielded EFs from 0.0 to 35.9 against 0.0 to 23.7 with band application. Under the same climate the EFs varied with the soil type and the management (crop and slurry aplication method). Globally, the sandy loam soil had higher EFs than the sandy soil, probably due to the longer periods with WFPS higher than 60% and its greater organic C availability. For each soil type, injection gave higher EFs than surface aplication due to the drastic reduction in volatilization - which left more N for N_2O production. The same tendencies were found by Velthof and Losada (2011) for soils in the Netherlands cultivated with maize.

Cayuela et al. (2017) recently published a meta-analysis of N_2O emissions, presenting an average overall EF for Mediterranean agriculture of 0.5%, which is substantially lower than the IPCC default value of 1%. When comparing irrigation methods/systems, drip irrigation systems had a 44% lower EF than sprinkler irrigation (0.91). These authors presented lower values for rainfed crops (0.27) than for irrigated crops (0.63). In the present study the rainfed crop had higher EFs than the irrigated crop for the sandy soil, while for the sandy loam soil the values were similar. It is of note that the irrigation system and its management greatly influenced the N losses and corresponding EFs. In this study the irrigation system tended to minimize losses since the crop requirements were carefully determined using historical data and the irrigation events were scheduled based upon crop evapotranspiration calculations and soil water measurements.

The surface band application of slurry produced average EFs for the double cropping system of 0.23% and 0.6% for the sandy and sandy loam soils, respectively. For the injection method, the corresponding values were 0.67% and 1.02%, respectively.

The standard deviations of the EFs (Fig. 9) indicate that the values varied considerably among years, probably according to the hydrologic conditions. This is confirmed in Fig. 10 and may be associated with the swapping of N losses among different compartments, as well as with

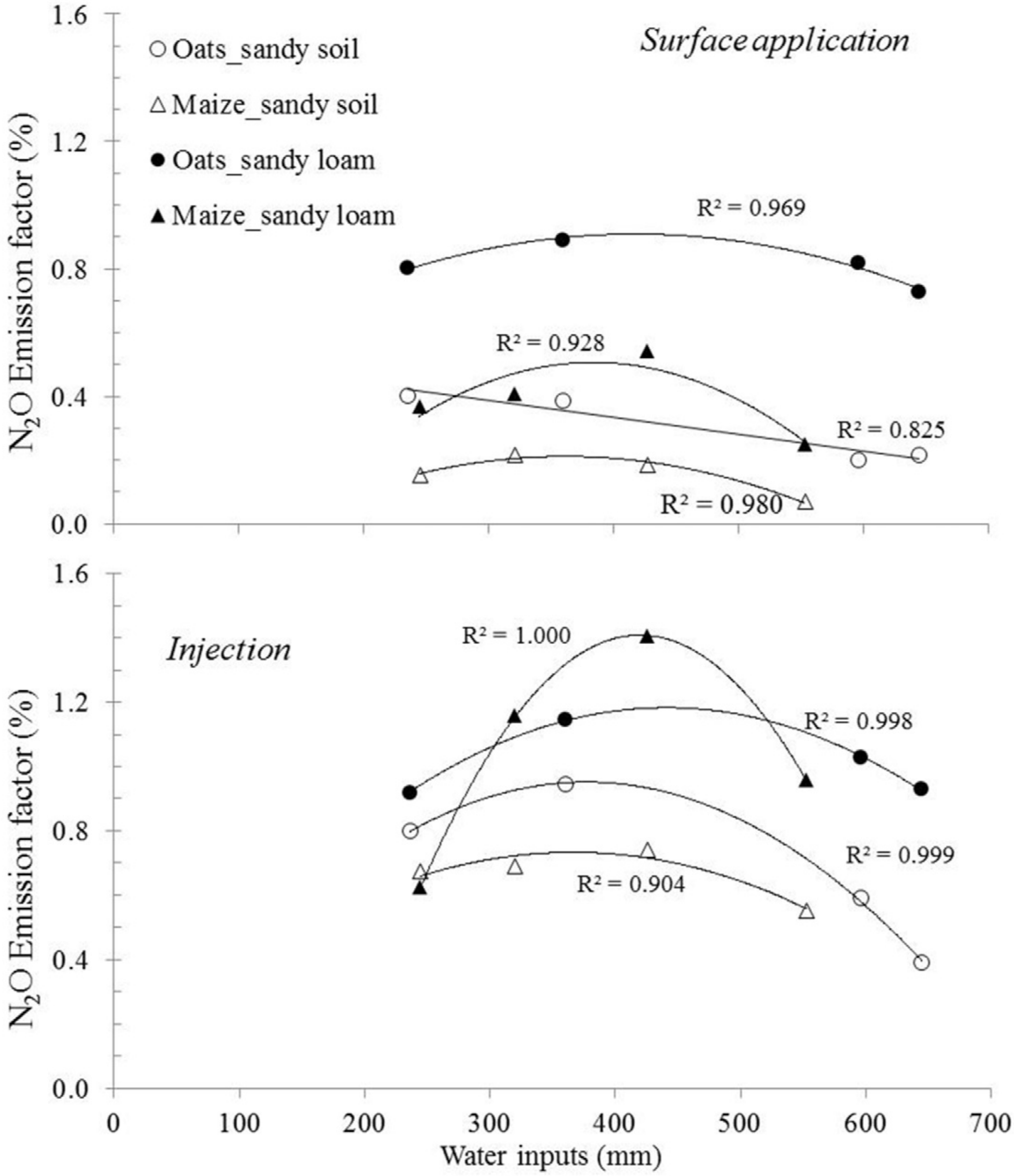

Fig. 10. Relationship between the N_2O emission and the water inputs through irrigation and precipitation.

the influence of soil moisture on the biochemical transformations of N and the diffusion within the soil to the surface. The EFs for the oats crop in the sandy loam soil decreased with the increase in the water input (Nevertheless, for the other situations, the EFs had an inverted parabola trend, indicating a threshold in the water input from which the EFs start to decrease. Trend is probably due to the fact that gas diffusion is slowed in soils with a higher water content, enabling NO to be further reduced to N_2O (Signor and Cerri, 2013). Considering that for the oats crop there was a gap from 350 to 600 mm, it is not possible to distinguish the thresholds for both soil types; but, for both, the EF was already lower for the 600 mm input. Higher EF values were found for the lowest rainfall of 410 mm during 2014–2015. More nitrification, less leaching, and hence more direct emissions of N_2O during this crop season could mean that nitrification was a bigger source of N_2O under the conditions studied.

The N pollution swapping, among the distinct loss pathways, found for the studied systems complicates the selection of the best slurry application practice. Indirect N_2O emissions from volatilization and NO_3^- leaching were then estimated using the IPCC default factors (0.1% for NH_3 volatilization and 0.75% for NO_3^- leaching), and then converted to carbon equivalent units (Table 6). For the sandy soil, from the environmental protection perspective and considering the global warming potential (GWP), band application of slurry seems to be the best option since it minimizes the total emissions (direct + indirect) in spite of

Table 6
Global warming potential (GWP) of direct and indirect N_2O emissions expressed as kg CO_2-eq/kg slurry.

	GWP emissions (as kg CO_2-eq/kg slurry)	
	Surface band application	Injection
Sandy soil		
Direct	89.0	253.6
Indirect	262.5	132.9
Total	351.5	386.5
Sandy loam soil		
Direct	319.2	421.4
Indirect	148.5	40.8
Total	467.7	462.2

the high contribution from N volatilization. For the sandy loam soil there is no difference between the application methods. However, as described in Sutton et al. (2011), NH_3 emissions negatively affect humans (respiratory diseases caused by fine particulate matter in the atmosphere) and ecosystems and biodiversity (e.g. acidification of soils and aquatic ecosystems and increased incidence of pests and diseases). According to the same authors, to these effects was assign maximum prioritization for future international action with respect to policies development and excessive N effects mitigation.

It is therefore necessary to revise some of the recommendations for manure application that suggest injection as the best option regardless of soils, crops and climatic conditions.

4. Conclusions

Given the challenges in fitting the model to such a comprehensive dataset, the RZWQM2 simulated well the fluxes of N to three environmental compartments (soil, air, and water), with the accuracy statistics having values within the expected ranges.

After being tested against four years of experimental data from field lysimeters, the model allowed the prediction of N_2O, NH_3, and NO_3^- emissions for the full double cropping season, including the non-growing periods. This information is highly relevant to target the mitigation strategies and improve EFs values.

For both soils, gas losses were higher during the maize crop season while leaching was higher for the oats season. The main difference when comparing surface band application of slurry and injection is that in the latter the gas losses are somewhat smaller, mainly due to the reduction in NH_4^+ volatilization. Nevertheless, while with surface application volatilization is the main N loss process, leaching becomes the prevalent process when the slurry is injected. This N swapping among path losses makes the selection of the best slurry application method difficult and thus the N mitigation measures must be targeted according to the environmental compartment showing the highest vulnerability.

Generally, the estimated EFs were lower than or (in the case of slurry injection in the sandy loam soil) equal to the IPCC default values. The average EFs for the double crop system varied between the rainfed and the irrigated crop and with the soil type, the slurry application method, and the hydrological year, reinforcing the need for site-specific EFs for the estimations instead of the IPCC default values.

Regarding the GWP emissions from direct and indirect N_2O production, surface application seems to be the best application method, particularly if the soil is very permeable. However, NH_3 emissions negatively affect humans, ecosystems and biodiversity (Sutton et al., 2011). Ultimately, the choice of the best practice should depend on the most vulnerable environmental compartment (soil/atmosphere/water bodies) of the agro-ecosystem under study and should consider a compromise between the environmental and agronomic objectives.

The methodologies used in the present study, based upon integrated systems modelling and focusing on scenario analysis, can support policy making as they can be used to set up integral strategies to decrease N emissions from livestock farming systems, taking into account possible synergies and antagonisms of mitigation measures regarding NH_3 and N_2O emissions and NO_3^- leaching.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.136596.

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