

Long-term analysis of soil water regime and nitrate dynamics at agricultural experimental site: Field-scale monitoring and numerical modeling using HYDRUS-1D

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ABSTRACT

Intensive agricultural practices increase agrochemical pollution, particularly nitrogen (N) based fertilizers, which present an environmental risk. This study aims to evaluate long-term (2009–2020) data on soil water regime and nitrate dynamics at an agricultural experimental site on fine-textured soils and to better understand the implications of N management in relation to groundwater pollution. The field site is located in the Bid field (eastern Croatia), in the proximity of the Sava river. Zero-tension lysimeters were installed at six selected locations. Lysimeters were used to monitor the water regime, i.e., outflows in which nitrate concentration was measured, while additional soil-water samples were collected via 4 and 15-meter-deep monitoring wells. Soil hydraulic parameters were estimated by combining the laboratory measurements, and estimation in RETC software. Water regime and nitrate leaching in lysimeters were simulated using HYDRUS-1D for each year to allow crop rotation and to evaluate their effects individually. The HYDRUS-1D model successfully reproduced lysimeter outflows and nitrate dynamics, which was confirmed with high R^2 values (water: 93% above 0.7, and nitrate: 73% above 0.7) indicating the good performance of the model simulating nitrification chain reactions. Principal component analysis (PCA) was performed to identify the relationships among all soil properties and environmental characteristics. The results showed the complex interaction of soil hydraulic properties, precipitation patterns, plant uptake, and N application. All locations have a decreasing trend of nitrate leaching over the investigation period. Most of the lysimeter outflows and elevated nitrate concentrations were connected to the wet period of the year when the soil was saturated, and evapotranspiration was low. The results of this study show that it is important to optimize N fertilizer applications for each particular environmental condition to reduce nitrate loss. The study indicates the importance of long-term field studies, key for agro-hydrological modeling and the improvement of agricultural practices.

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1. Introduction

While field conditions such as fine texture (Aulakh et al., 1992), shallow groundwater (Spalding and Parrott, 1994), and high soil water content (Abbasi and Adams, 2000) favor denitrification rates, the consideration of N leaching harmful effects provoked by the uncertainty of the application rates of N in such agricultural area cannot be neglected (Miller et al., 2020). High annual precipitation increases plants' N uptake and the dilution effect, reducing nitrate concentration, as well as higher annual temperatures can, as evapotranspiration rates increase (Wick et al., 2012). However, nitrate, is one of the first nutrients to be washed from the soil profile due to its high mobility (Colombani et al., 2020). The rhizosphere dynamics of nutrients is multifactorial as it depends on plant characteristics and water demands, while several factors cannot be accurately quantified due to spatio-temporal variability. Nitrate does bind onto clay or organic compounds, increasing the losses by leaching or overland flow and surface water and groundwater pollution (Ravikumar et al., 2011). N management in several parts of the world is still challenging and should be approached multi-methodically to enhance N use efficiency and decrease losses (Sharma and Bali, 2017; Snyder, 2017; Yang et al., 2022).

Among all N management factors that influence nitrate losses, the application of the proper fertilizer rate with timing remains the most relevant (Banger et al., 2020; Gao et al., 2018; Li et al., 2019). To apply the proper amount, several factors need to be considered, such as particle size distribution (Cambouris et al., 2016), organic matter content (van Vliet et al., 2007), cropping rotation (Helmers et al., 2012), tillage system (Wang et al., 2015), crop yield (Srivastava et al., 2018), profit calculation (Lv et al., 2015) and the impact on the environment (Zhang, 2015). Linking management tools with precision technologies (Cao et al., 2012), information systems (Tripathi et al., 2017), crop growth, N utilization and transformation models (Kersebaum, 2007), weather models (Anderson and Kyveryga, 2016), and agro-hydrological models (Bouadi et al., 2017), may improve and optimize N management. Correctly calibrated and validated models are key for farmers and policymakers to establish proper agricultural practices (Groenvelde et al., 2021). Connecting field data with modeling approaches into long-term studies of water regime and N cycle with the focus on meteorological events as drivers has produced quality outlooks on the N efficiency and environmental impact (Crossman et al., 2016; Motarjemi et al., 2021; Sun et al., 2018). Hydrological numerical models are a useful tool for nitrate leaching risk prediction for surface water and groundwater pollution (Martin del Campo et al., 2021; Miller et al., 2020; Zhu et al., 2021). One of the most often applied models, HYDRUS (Šimůnek et al., 2016b) can be used to model water movement (Kassaye et al., 2021), deep percolation (Beyene et al., 2018), nitrate leaching (Zhang et al., 2020), or N uptake (Li et al., 2015) at field scale. HYDRUS-1D model application can support N management (Shahrokhnia and Sepaskhah, 2018) and assess the impact on the water quality (Zhang et al., 2020).

Investigating water and solute fluxes by water collection from undisturbed soils is a complex undertaking. For in-situ soil water sampling, methods such as suction cups, plates, capillary wicks and lysimeters are widely used (Groh et al., 2018; Schmidt and Lin, 2008; Shen and Hoffland, 2007). One of the lysimeter techniques used, due to its practical and inexpensive nature is the zero-tension plate lysimeter method. They can generate valuable data by simulating actual field conditions (Groffman et al., 2009; Filipović et al., 2013a, 2013b; Tiefenbacher et al., 2020). The information obtained by the zero-tension plate lysimeters, which varies depending on the field situation and local, expresses the leaching depth and exhibits more solute spreading than suction plates, thus reflecting suitably for ecosystem input-output budgets (Marques et al., 1996; Kasteel et al., 2007;). Also, previous works captured the rainfall intensity impacts on organic solute leachate into subsoil using this technique (Kaiser and Guggenberger, 2005). However, there are several limitations, since they have only the capability of collecting water when the soil is in a positive pressure state or the water

may diverge from the instrument towards the dryer surrounding soil (Zhu et al., 2009). This can result in low leachate catchment efficiency (Jemison and Fox, 1992). However, zero-tension plate lysimeters work efficiently in soil conditions near the saturation point (Peters and Durner, 2009). Hence, an adequate evaluation requires field data collection for data generation. Nevertheless, in nitrate transport and leaching assessment, often multiyear data collected systematically at an investigated site is lacking, thus preventing researchers from having decisive conclusions that have merit. Multiyear data is often crucial for agricultural research, due the fields nature of spatial and temporal variability (Blasch et al., 2020; Dang et al., 2011).

The presented study combines long-term field data collection with including real agricultural field conditions allowing multi-crop rotation and combining it with extensive water and N transformation modeling tools. Therefore, the aims of this study were: i) to evaluate long-term (12 years; 2009–2020) data on soil water regime and nitrate dynamics in the vadose zone of an intensive agricultural managed area (at six locations) located in eastern Croatia, ii) to combine the numerical water flow and nitrification chain models with laboratory and field obtained data by considering farmers' N management practices, crop rotation, soil, and climate data into account, and iii) to test if the agro-hydrological model can generate insights to improve the N management decision making.

2. Materials and methods

2.1. Experimental site and soil-water sampling

The research area (Fig. 1) is located in the Bid field in eastern Croatia (18° 25' to 18° 33' E; 45° 07' to 45° 11' N). The experimental study was carried out during 2009–2020. Daily meteorological data was collected from a meteorological station in close proximity of the investigated area (45° 09' N and 18° 42' E). Long-term (1981–2020) average annual precipitation and temperature are 685 mm and 11.9 °C, respectively.

Zero-tension lysimeters (round, \varnothing 0.5 m, height 0.05 m) were installed at the six selected locations (L1 – L6) (lysimeters at L6 installed in 2015), in pairs to allow repetitions in sampling. A vertical trench was excavated to 2 m with an unearthen horizontal slot at a depth of 0.5 m. The installation depth was selected using the following criteria: varying local groundwater levels, implementation of applied agro-technical management (e.g., tillage), and the average depth of the main root mass in the crop rotation. A round lysimeter plate, filled with disturbed soil material (horizon of installation), was inserted into the slot to retain the soil above the lysimeter undisturbed. A PVC net was applied on the lysimeter plate surface for filtering purposes to prevent small particles from being washed out with the leachate. Outflow pipes were installed and connected to soil water containers placed at the edge of the field to allow unobstructed access for sample collection. Leachate was collected according to significant precipitation events throughout the years. For soil-water sampling from deeper layers, at each location, 4 and 15-meter-deep monitoring wells, perforated at the bottom, were installed nearby the zero-tension lysimeters (Fig. 2). Soil water samples in replicates (2x) were taken from zero-tension lysimeters and monitoring wells (no replicates), corresponding to the moisture conditions in the field. Concentrations of NO_3^- (and NH_4^+ , presented as [supplement data](#)) were determined (ISO 13395:1998) by a continuous flow auto-analyzer (San++ Continuous Flow Analyzer, Skalar). All samples were filtered through 0.45 μm membrane filters and stored for up to 2 days at 4 °C without acid preservation to reduce the potential interference of the dissolved organic matter.

The main field crops cultivated during the 12-year research period at investigated locations (L) were: Alfalfa (*Medicago sativa* L.), Barley (*Hordeum vulgare* L.), Maize (*Zea mays* L.), Oat (*Avena sativa* L.), Rapeseed (*Brassica napus* L.), Soybean (*Glycine max* L.), Spelt (*Triticum spelta* L.), Sugar beet (*Beta vulgaris* L.), Sunflower (*Helianthus annuus* L.), Triticale (\times *Triticosecale*), Wheat (*Triticum aestivum* L.) and grass mixture. The field data was collected without interfering with standard



Fig. 1. Location of the experimental site in eastern Croatia and positions of the water collection instruments in the Bid field (L1-L6).

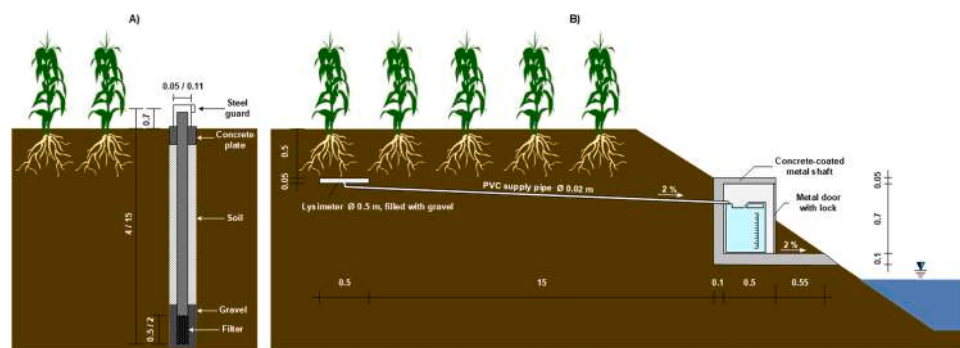


Fig. 2. Scheme of A) installed monitoring wells for soil-water sampling at 4 and 15 m and B) installed zero-tension lysimeter system at 0.5 m depth at the experimental site in Eastern Croatia (Bid field; the scheme is not fully to scale).

Table 1

Crop rotations, fertilizer input (N in) and number of lysimeter observations (n) at investigated locations (L1-L6) during the research period (2009–2020).

	L1		L2		L3		L4		L5		L6		Obs. points (n)
Year	Crop	N/in [kg ha ⁻¹]	Crop	N/in [kg ha ⁻¹]	Crop	N/in [kg ha ⁻¹]	Crop	N/in [kg ha ⁻¹]	Crop	N/in [kg ha ⁻¹]	Crop	N/in [kg ha ⁻¹]	
2009	Wheat	205	Maize	240	Wheat	130	–	Maize	350	–	–	–	7
2010	–	Barley	90	Maize	225	Maize	170	Maize	325	–	–	–	10
2011	Barley	45	Maize	230	–	–	–	–	–	–	–	–	5
2012	–	–	Maize	270	Maize	205	–	–	–	–	–	–	6
2013	Oat	153	–	Maize	185	–	–	–	–	–	–	–	6
2014	Soybean	140	Alfalfa	0	Grass mixture	135	Barley	80	Maize	120	–	–	10
2015	Soybean	80	Soybean	0	Maize	155	Wheat	90	Maize	170	Alfalfa	90	7
2016	Oat	49	Spelt	54	Barley	323	Rapeseed	100	Barley	222	Wheat	120	8
2017	Rapeseed	150	Soybean	*	Alfalfa	*	Barley	210	Sugar beet	115	Maize	185	4
2018	Soybean	38	Soybean	46	Alfalfa	*	Rapeseed	125	Sunflower	72	Soybean	105	5
2019	Maize	116	Triticale	54	Alfalfa	0	Wheat	81	Sugar beet	131	Wheat	150	6
2020	Soybean	45	Soybean	0	Alfalfa	0	Maize	185	Barley	262	Rapeseed	40	8

*represents that unknown characteristics of organic fertilizer have been used at the study location.

–represents missing field data provided by the farmers or no crop production at the investigated year/site.

agricultural management implemented by farmers (Table 1). The detailed fertilizer information can be found in Table S1.

2.2. Soil parameters

The study was performed at six selected locations, representing the dominant soil types in that area (gley soils). Soils were classified according to the World Reference Base for Soil Resources (Anon, 2014): Luvic Stagnic Phaeozem Siltic (Horizons: Ap-Bt-Bg-C) locations L1, L2, and L6, Haplic Fluvisol Eutric Siltic (Horizons: Ap-A/Bw-Cg-Cr) location L3, and Haplic Gleysol Calcaric Eutric Siltic (Horizons: Ap-Bg-Cr-Cg) location L4 and L5. The soil analysis was conducted in 2009. For the soil particle size distribution analysis, disturbed soil samples were sampled from the six locations in three repetitions, and multiple depths (as specified in Table 2). The soil particle size distribution analysis was determined by combined sieving and sedimentation (ISO 11277:2009). For the measurements of bulk density and the soil hydraulic properties at L1–L6 locations, undisturbed soil samples (100 cm³) were taken from the first two soil horizons (depths for each location specified in Table 2). The saturated hydraulic conductivities (K_s) were measured using the constant head method (Klute and Dirksen, 1986). The saturated water content (θ_s) was measured using a saturation pan, and the points of the soil water content of the soil water retention curve (SWRC) were measured using a pressure plate apparatus (Dane and Hopmans, 2002) with applied pressure heads of 33 (field capacity), 625 and 1500 (wilting point) kPa. The particle size distribution was determined using the combination of sieving and sedimentation procedure, according to Gee and Or (2002). The basic physical soil properties are presented in Table 2.

2.3. Water flow modeling

Water flow was simulated using the HYDRUS-1D software (Šimůnek et al., 2016b). For the simulation of water flow in a one-dimensional profile, the Richards equation for the variably saturated porous medium was used:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} K \left(\frac{\partial h}{\partial z} + 1 \right) - S \quad (1)$$

where θ is volumetric soil water content [L³ L⁻³], h is pressure head [L], K is hydraulic conductivity of unsaturated soil [L T⁻¹], z is gravitational head [L], t is time [T], and S is a sink term for root water uptake [T⁻¹].

Soil hydraulic functions were described using the van Genuchten-Mualem single porosity model (van Genuchten, 1980):

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{(1 + |\alpha h|^n)^m} \quad \text{for } h < 0 \quad (2)$$

$$\theta(h) = \theta_s \quad \text{for } h \geq 0 \quad (3)$$

$$K(h) = K_s S_e^l (1 - (1 - S_e^{\frac{1}{n}})^m)^2 \quad (4)$$

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} \quad (5)$$

$$m = 1 - \frac{1}{n}; n > 1 \quad (6)$$

where $\theta(h)$ is volumetric water content [L³ L⁻³], $K(h)$ is hydraulic conductivity of unsaturated soil at the water pressure head of h [L], θ_r is residual soil-water content [L³ L⁻³], θ_s is water content in saturated soil [L³ L⁻³], S_e is the effective saturation, K_s is the saturated hydraulic conductivity of the soil [L T⁻¹], α is the inverse of air-entry value (bubbling pressure), n is the dimensionless soil pore size distribution index, m is the dimensionless optimization coefficient, and l is the pore connectivity parameter [-].

While saturated water content, θ_s , and the hydraulic conductivity, K_s , were measured, other parameters that describe the soil water retention curve (α and n) were estimated from the parameters in Table 2 using the RETC module (Šimůnek et al., 2016a). Pore connectivity parameter, l , was set to 0.5 as found valid for most soil types (Mualem, 1976). Residual water content, θ_r , was set at 0 for all locations, and due to good concordance of the optimization results, its small influence on total water retention was confirmed (Šimůnek et al., 1998; González et al.,

Table 3

Optimized soil hydraulic parameters (RETC) used for numerical simulations and parameters obtained by laboratory methods (θ_s , K_s) for soils at selected locations (L1–L6) at Bid experimental field (eastern Croatia).

	Depth (cm)	θ_r (cm ³ cm ⁻³)	θ_s (cm ³ cm ⁻³)	K_s (cm day ⁻¹)	α (cm ⁻¹)	n (-)
L1	0–40	0.0	0.38	11	0.00261	1.18
	40–75	0.0	0.37	15	0.00263	1.17
L2	0–30	0.0	0.36	17	0.0018	1.26
	30–75	0.0	0.37	12	0.00017	1.25
L3	0–40	0.0	0.37	14	0.00158	1.20
	40–90	0.0	0.38	9	0.00285	1.18
L4	0–25	0.0	0.40	12	0.00032	1.19
	25–80	0.0	0.41	10	0.0527	1.17
L5	0–30	0.0	0.42	12	0.00136	1.20
	30–70	0.0	0.41	14	0.00212	1.17
L6	0–30	0.0	0.43	16	0.01241	1.19
	30–70	0.0	0.44	12	0.05525	1.17

Table 2

Particle size distribution, saturated water content (θ_s), bulk density, hydraulic conductivity (K_s), water retention at selected pressure points, and texture at six locations (L1–L6) at Bid experimental site in Croatia ($n = 3$).

Location	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Texture	θ_s (cm ³ cm ⁻³)	Soil bulk density (g cm ⁻³)	K_s (cm day ⁻¹)	Water retention at pressure (kPa)		
									33	625	1500
L1	0–40	13	65	22	Silt Loam	0.38	1.59	11	0.34	0.22	0.20
	40–75	4	63	33	Silty Clay Loam	0.37	1.57	15	0.34	0.22	0.20
L2	0–30	9	67	24	Silt Loam	0.36	1.56	17	0.33	0.17	0.16
	30–75	2	61	37	Silty Clay Loam	0.37	1.55	12	0.39	0.31	0.28
L3	0–40	6	60	34	Silty Clay Loam	0.37	1.49	14	0.35	0.22	0.19
	40–90	6	60	34	Silty Clay Loam	0.38	1.55	9	0.34	0.22	0.19
L4	0–25	3	56	41	Silty Clay	0.40	1.47	12	0.41	0.32	0.29
	25–80	2	57	41	Silty Clay	0.41	1.46	10	0.35	0.22	0.20
L5	0–30	5	54	41	Silty Clay	0.42	1.37	12	0.39	0.28	0.22
	30–70	3	54	43	Silty Clay	0.41	1.55	14	0.37	0.27	0.21
L6	0–30	5	75	20	Silt Loam	0.43	1.56	16	0.29	0.22	0.17
	30–70	7	73	20	Silt Loam	0.44	1.39	12	0.29	0.22	0.17

2015). Optimized and measured soil hydraulic parameters are shown in Table 3.

Boundary conditions were set as follows. The atmospheric conditions (daily data) with surface runoff were selected at the top, while the seepage face was applied for the bottom. Domain discretization density was increased near the soil surface while the whole profile had 101 nodes. Initial conditions of simulations were set according to measured field pressure head data determined in nearby piezometers, at the start of each year. The potential evapotranspiration, determined using the Penman–Monteith equation (Allen et al., 1998) and the crop coefficient, was divided into the potential evaporation and transpiration using Leaf Area Index (LAI) (Li et al., 2014). Literature plant parameters (LAI, plant height, albedo) were used as input parameters (Breuer et al., 2003) for the model. Root water uptake was simulated using the approach of Feddes et al. (1978). The calculated potential transpiration flux was then converted into actual root water uptake by combining the piecewise linear water stress response model proposed by Feddes et al. (1978) (parameters: $P0$ [L], $POpt$ [L], $P2H$ [L], $P2L$ [L], $P3$ [L]) and a root density function that accounts for the root density and growth (e.g., Brunetti et al., 2019, 2021).

2.4. Nitrate transport modeling

HYDRUS allows the simulation of multiple solutes that are subject to first-order degradation reactions (nitrogen species). The first-order decay chain of urea (Tillotson et al., 1980) consists of a reaction pathway that involves the hydrolysis of urea by heterotrophic bacteria to form ammonium, and the subsequent nitrification of ammonium by autotrophic bacteria to form nitrite and nitrate. The resulting di-nitrogen is denitrified to form N_2 and N_2O . For the simulations of the nitrification chain reactions in soil, parameters for all investigated locations were set as follows. The first-order reaction term representing nitrification of urea or KAN fertilizer to ammonium (μ_a), was set at 0.38 day^{-1} , while the first-order reaction term representing nitrification of ammonium to nitrate (μ_n) was set at 0.2 day^{-1} (Hanson et al., 2006; Li et al., 2015; Ramos et al., 2012). The distribution coefficient for ammonium (K_d) was assumed to be $3.5 \text{ cm}^3 \text{ g}^{-1}$ (Hanson et al., 2006; Filipović et al., 2013a, 2015, 2013b). The initial ammonium and nitrate contents in soils were set according to the first measured N concentrations of the zero-tension lysimeter in a year. Application of NPK fertilizer, which was defined also in kg ha^{-1} , was transformed into the concentration of N for both species (ammonium or nitrate) in measured/applied precipitation (mmol cm^{-3}) assuming the share of each species (9% of NH_4^+ , 6% of NO_3^-) in the fertilizer, the volume of water per hectare and the molar mass of the species (0.018 for NH_4^+ and 0.062 for NO_3^-). Unlimited passive uptake of NH_4^+ and NO_3^- in the liquid phase was considered (Li et al., 2015). The effect of denitrification was neglected due to the presence of high unsaturated conditions in the first 50 cm where the modeling was performed.

To solve the transport of each separate chemical partial (urea, ammonium, and nitrate), the following equations were used:

For UREA:

$$\frac{\partial \theta c_1}{\partial t} = \nabla (\theta D \nabla c_1) - \nabla (q c_1) - \mu_a \theta c_1 - S_w c_1 \quad (7)$$

For ammonium:

$$\frac{\partial \theta c_2}{\partial t} + \rho \frac{\partial s_2}{\partial t} = \nabla (\theta D \nabla c_2) - \nabla (q c_2) - \mu_v \theta c_2 - \mu_n \theta c_2 + \mu_a \theta c_1 - S_w c_2 \quad (8)$$

For nitrates:

$$\frac{\partial \theta c_3}{\partial t} = \nabla (\theta D \nabla c_3) - \nabla (q c_3) + \mu_n \theta c_2 - S_w c_3 \quad (9)$$

where c_i is the liquid phase concentration of the chemical species i (subscripts 1, 2, and 3 represent urea, ammonium, and nitrate,

respectively) [M L^{-3}], D is the dispersion coefficient tensor [$\text{L}^2 \text{ T}^{-1}$], q is the volumetric flux density [L T^{-1}], ρ is the bulk density of the soil [M L^{-3}], s_2 is the adsorbed concentration of ammonium [M M^{-1}], μ_a is the first-order reaction rate constant [T^{-1}] representing nitrification of urea to ammonium, μ_v is the first-order reaction rate constant [T^{-1}] representing volatilization of ammonium to ammonia, μ_n is the first-order reaction rate constant [T^{-1}] representing nitrification of ammonium to nitrate and S_w is a sink term accounting for plant water uptake [T^{-1}].

The relationship between ammonium in solution (c_2) and adsorbed (s_2) is described as follows:

$$s_2 = K_d c_2$$

where K_d is the distribution coefficient for ammonium [$\text{L}^3 \text{ M}^{-1}$].

2.5. Model validation

Model validation was carried out with the coefficient of determination (R^2), the root mean square error (RMSE) and the mean absolute error (MAE):

$$R^2 = \left[\frac{\sum_{i=1}^N (O_i - \bar{O})(P_i - \bar{P})}{\left[\sum_{i=1}^N (O_i - \bar{O})^2 \right]^{0.5} \left[\sum_{i=1}^N (P_i - \bar{P})^2 \right]^{0.5}} \right]^2 \quad (10)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^N (P_i - O_i)^2}{N}} \quad (11)$$

$$MAE = \frac{\sum_{i=1}^N |P_i - O_i|}{N} \quad (12)$$

where O_i is observation, P_i is prediction, \bar{O} is average observation and \bar{P} is average prediction, while the N is the sample size.

2.6. Statistical analysis

Principal component analysis (PCA) was performed, based on the correlation matrix, to identify the relationships among all soil properties and environmental characteristics (annual precipitation, evapotranspiration) for a) all years (crops) and for individual grouping according i.e. combined dataset; b) maize; and c) cereal prevalence in crop rotation. The maize and cereal groups were selected due to the largest occurrence in crop rotation during the 12 years. The logarithmically transformed data were used for the PCA since it was the closest to normality. The PCA analyses were performed using Statistica 12.0 for Windows (StatSoft, Tulsa, USA).

3. Results & discussion

3.1. Model validation

Results of the model validation are presented in Table 4, using the goodness of fit coefficient of determination (R^2) analysis. R^2 for water flow simulations range from 0.58 to 0.97 (Table 4), while R^2 values of nitrate simulations were 0.12–0.97 (Table 4). 93% of R^2 values for water flow simulations exceeded the value of 0.7, whereas nitrate simulations had lower values, being 73% above 0.7, and can be perceived as a satisfactory outcome for the described modeling (Moriassi et al., 2015), while also indicating the occurrence of greater uncertainty in nitrate modeling, as expected due to the larger parameter input. One of the lowest values of R^2 for water flow simulations occurred in 2011 ($L1 = 0.64$, $L2 = 0.62$), and can be linked to a low number of observations ($n = 5$) caused by drought during this dry year (393.6 mm).

Table 4

Coefficients of determination (R^2), root mean square error (RMSE) and mean absolute error (MAE) for simulated vs observed zero-tension lysimeter: soil-water outflows and nitrate outflows during 2009 – 2020 at the experimental site.

		Location	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020
Soil-water outflows	R^2	L1	0.95	–	0.64	–	0.87	0.90	0.94	0.90	0.89	0.92	0.58	0.86
		L2	0.93	0.90	0.62	–	–	0.93	0.94	0.89	0.87	0.94	0.74	0.84
		L3	0.93	0.93	–	0.78	0.88	0.94	0.85	0.90	0.82	0.91	0.72	0.97
		L4	–	0.92	–	0.83	–	0.96	0.95	0.96	0.80	0.93	0.77	0.88
		L5	0.91	0.97	–	–	–	0.89	0.95	0.87	0.72	0.94	0.84	0.67
		L6	–	–	–	–	–	–	0.80	0.88	0.87	0.96	0.70	0.85
	RMSE	L1	5.31	–	1.94	–	14.55	4.86	4.00	4.14	1.05	9.83	3.11	3.57
		L2	5.69	4.04	2.05	–	–	3.07	3.70	4.27	2.49	14.00	3.97	4.98
		L3	2.69	10.05	–	4.14	15.76	3.22	4.37	3.30	0.70	2.89	8.20	3.03
		L4	–	12.33	–	2.31	–	2.59	1.11	2.46	1.38	1.59	6.35	4.82
		L5	3.36	8.05	–	–	–	4.73	1.52	5.27	2.02	8.94	2.83	7.01
		L6	–	–	–	–	–	–	3.40	4.77	3.60	5.77	7.19	4.95
	MAE	L1	4.69	–	1.87	–	13.50	4.13	3.09	3.04	0.71	9.00	2.57	2.90
		L2	5.12	3.54	1.89	–	–	2.46	2.75	3.40	2.25	12.48	3.33	4.10
		L3	2.32	7.90	–	3.89	14.52	2.64	3.11	2.86	0.59	2.46	6.87	2.61
		L4	–	8.61	–	2.24	–	2.03	0.82	2.15	1.33	1.45	5.54	3.60
		L5	2.93	7.81	–	–	–	4.14	1.07	4.65	1.71	7.50	2.19	5.78
		L6	–	–	–	–	–	–	2.72	4.31	3.45	4.79	6.11	4.09
Nitrate outflows	R^2	L1	0.90	–	0.54	–	0.91	0.95	0.59	0.56	0.81	0.70	0.75	0.84
		L2	0.83	0.75	0.53	–	–	0.51	0.85	0.52	*	0.68	0.75	0.87
		L3	0.94	0.83	–	0.76	0.75	0.89	0.91	0.81	*	*	0.12	0.97
		L4	–	0.87	–	0.71	–	0.72	0.62	0.90	0.65	0.97	0.36	0.90
		L5	0.88	0.82	–	–	–	0.76	0.87	0.84	0.75	0.80	0.62	0.79
		L6	–	–	–	–	–	–	0.89	0.61	0.73	0.80	0.31	0.87
	RMSE	L1	0.0412	–	0.0026	–	0.0221	0.0192	0.0011	0.0025	0.0005	0.0001	0.0004	0.0007
		L2	0.0103	0.0991	0.0026	–	–	0.0060	0.0007	0.0055	*	0.0010	0.0036	0.0005
		L3	0.0087	0.0083	–	0.0045	0.0322	0.0081	0.0013	0.0016	*	*	0.0004	0.0013
		L4	–	0.0132	–	0.0193	–	0.0080	0.0043	0.0011	0.0006	0.0061	0.0010	0.0009
		L5	0.0213	0.0232	–	–	–	0.0124	0.0004	0.0014	0.0023	0.0003	0.0032	0.0016
		L6	–	–	–	–	–	–	0.0004	0.0017	0.0013	0.0008	0.0007	0.0025
	MAE	L1	0.0248	–	0.0025	–	0.0182	0.0148	0.0008	0.0014	0.0004	0.0001	0.0004	0.0007
		L2	0.0092	0.0946	0.0026	–	–	0.0041	0.0005	0.0031	*	0.0010	0.0030	0.0005
		L3	0.0069	0.0081	–	0.0043	0.0274	0.0066	0.0012	0.0011	*	*	0.0003	0.0012
		L4	–	0.0125	–	0.0178	–	0.0060	0.0023	0.0008	0.0005	0.0047	0.0009	0.0007
		L5	0.0178	0.0224	–	–	–	0.0087	0.0004	0.0008	0.0023	0.0003	0.0029	0.0012
		L6	–	–	–	–	–	–	0.0003	0.0012	0.0012	0.0007	0.0007	0.0023

*represents that simulations were not carried out due to unknown characteristics of organic fertilizer used at the study locations.

- represents that simulations were not carried out due to missing field data provided by the farmers or no crop production.

Consequently, nitrate outflow simulations at the same locations resulted in lower R^2 as well ($L1 = 0.54$, $L2 = 0.53$). Water flow and nitrates simulations were more precise in wet years due to more observation points. The lowest value of R^2 for nitrate simulations occurred in 2019, at location L3 (0.12) where no nitrogen fertilizer was applied, and very low nitrate values were measured. RMSE ranged from 0.7 to 15.8 for water flow, while MAE showed similar range as well (0.59 – 14.5). Nitrate outflow RMSE and MAE averaged 0.008 and 0.007, respectively. It should be noted that zero-tension lysimeters also have some limitations in the precise quantification of soil water fluxes (Zhu et al., 2009), thus additionally supporting the field-derived data with numerical modeling is needed, especially in agricultural soils where nonlinear processes are present (Guo and Lin, 2018).

Altogether, these data deviations can be partially explained by soil heterogeneity, neglected the effect of soil structure in heavily managed agro-eco-systems, nonuniform rainfall and fertilizer distribution, and over- or under- estimation of crop uptake or N transformation parameters. Brunetti et al. (2021) performed a global sensitivity analysis after HYDRUS-1D model calibration on important factors driving the leaching of nitrate from Green Roofs. It was found that the first-order degradation coefficients had an appreciable impact on nitrate leaching together with organic N production rate and Feddes' parameter (P_0). The study focused on organic N transformations from wastewater application. In the current study, we only focused on inorganic N from application from fertilizers which have more consistent N transformation rates as their content is precisely controlled. In-depth analyses and focused experiments are recommended concerning rainfed open field agriculture in which precipitation can affect N turnover by increasing the nitrate

leaching potential and soil moisture. This influences microbial degradation processes (e.g., Maenhout et al., 2018), such as nitrification and denitrification due to aerobic–anaerobic cycles i.e., local soil moisture dynamics (Becker et al., 2007; Linquist et al., 2011; Qiu et al., 2020) or due to effect of dissolved organic carbon from plant residues (Surey et al., 2020).

3.2. Simulation and monitoring results: water flow and nitrogen dynamics

In the years with higher-than-average precipitation (> 685 mm), nitrate concentrations in lysimeters increased, pointing to a nitrate flushing from the soil (Fig. 3). As an input supplying the groundwater recharge, the precipitation initiates the water flow processes, causing water to flow either laterally to an adjacent area or vertically through the soil profile into groundwater, consequently repositioning the applied fertilizers. The other impact of precipitation on soil hydrology indicated that bulk precipitation can contribute significantly to macropore flow thus leading to the increased N losses. Furthermore, as Sigler et al. (2020) demonstrated in their simulations that over half of the nitrate leaching in a 14-year model was triggered in only two years by high-intensity precipitation events in that period. Similarly, Zheng et al. (2020) identified that land use and extreme precipitations were the main factors that controlled nitrate accumulation, leaching, and concentration in groundwater, in an intensively used agricultural area. However, this feedback mechanism in the vadose zone is complicated and requires models or multiple methods to assess and confirm. Firstly, the different rainfall intensities (e.g., rain splash) will alter the soil structure by influencing its vertical heterogeneity, leading to the inadequate

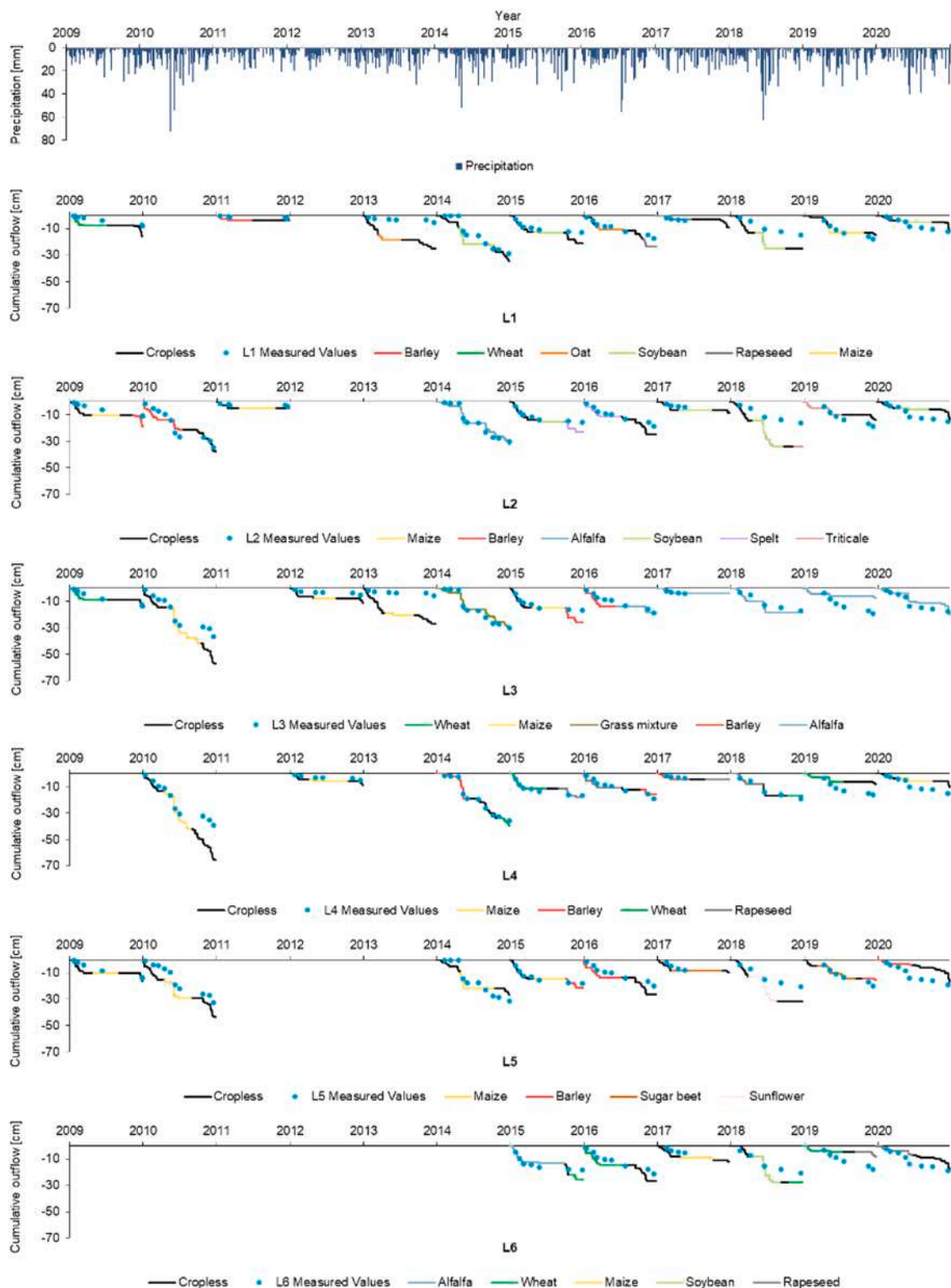


Fig. 3. Measured (blue dots) and simulated (black and colored lines) water outflow [cm] with H1D for lysimeters with daily precipitation [mm] during 2009–2020, at the investigated locations (L1 - L6). Black lines represent cropland simulations, while colored lines represent crop simulations.

dynamic simulation without some simple representation of soil vertical variability (Turkeltaub et al., 2021). Secondly, groundwater depth fluctuation caused by precipitation will also play an important role in N transportation (Bian et al., 2021). Beyond that, at higher clay content, a higher water outflow (Fig. 3) and nitrate concentration (Fig. 4) were generally observed. This could be connected to preferential flow, due to a higher likelihood of crack formation (vertic properties) in soils with

higher clay content (Oostindie and Bronswijk, 1995), and conditioned by the rate and timing of the fertilizer application (Amanullah, 2016).

The average evapotranspiration (ET) for all locations in the investigated period was 930.7 mm. The highest ET (1557 mm) was calculated for maize in 2017 (Fig. 5). Evapotranspiration impacted the measured water and nitrate outflow, with a general relation of high outflow and nitrate concentrations in years of low annual ET, and vice versa. The soil

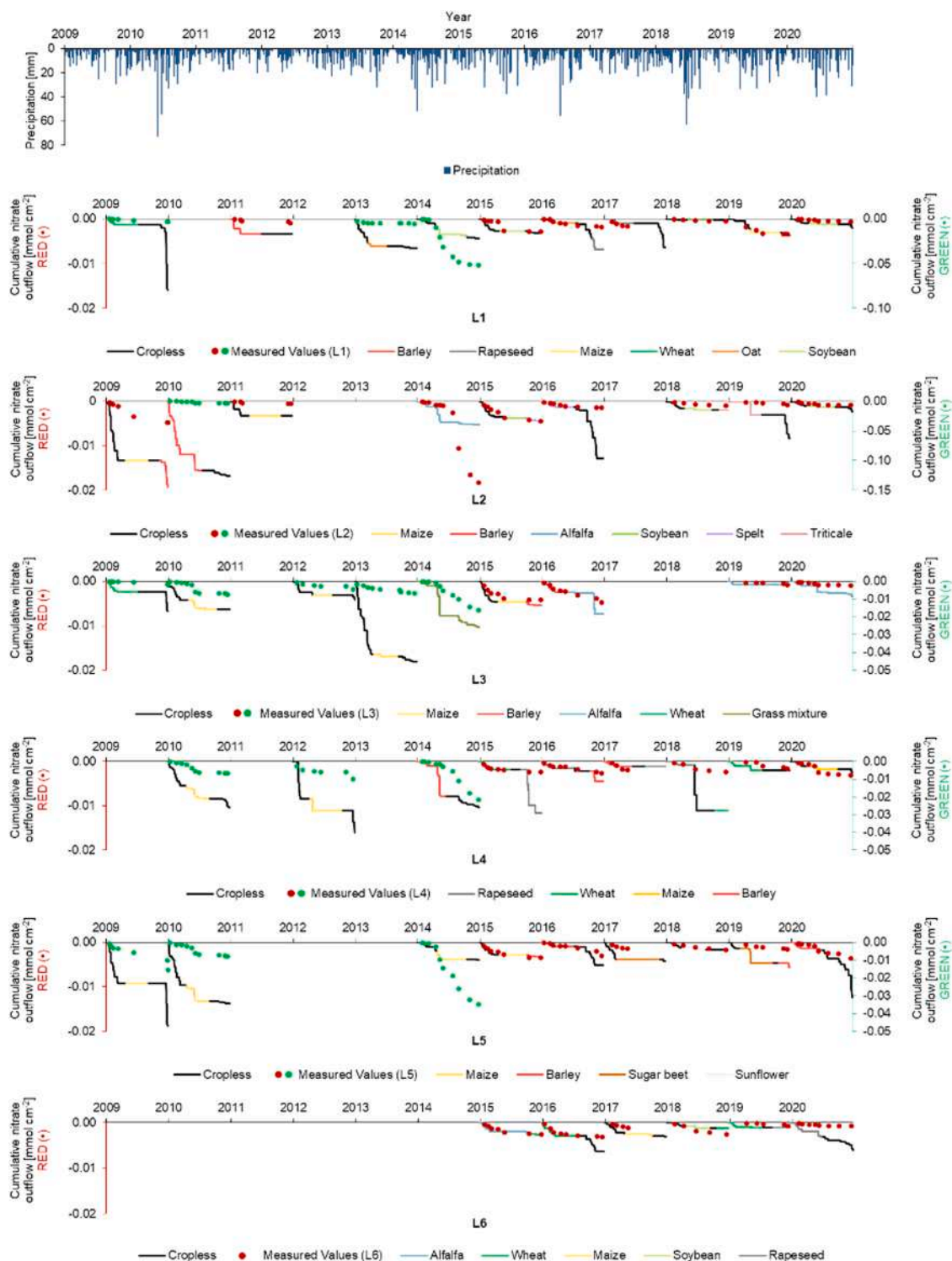


Fig. 4. Measured (red and green dots) and simulated (black and colored lines) cumulative nitrate outflow [mmol cm^{-2}] with H1D for lysimeters with daily precipitation [mm] during 2009–2020, at the investigated locations (L1 - L6). Black lines represent cropless simulations, while colored lines represent crop simulations. Scales differ within graphs for better data visualization (red dots – left axis / green dots – right axis).

hydrology may respond more sensitively to discharge than to increased ET related to warm temperature (Livneh et al., 2015). However, ET plays an important role in the N plant uptake rate. Average total N leaching (on all investigated locations) was 14% (Fig. S1), while the highest average in the year 2014 with 42%. Yan et al. (2021) highlighted that different irrigation amounts, based on ET values, in interaction with fertilization rates will significantly affect the N accumulation.

Otherwise, the increased ET was expected to decline the N loading due to a low-oxygen induced reduction of the nitrification (Jeppesen et al., 2011). On average, 54% of nitrate leaching occurred under some crop, while the highest average nitrate leaching during the cropless season occurred at L5 (60%) (Fig. S2). Lacerda et al. (2016) demonstrated that reducing N application based on the decrease in ET is an effective strategy to reduce the risk of groundwater contamination by nitrate

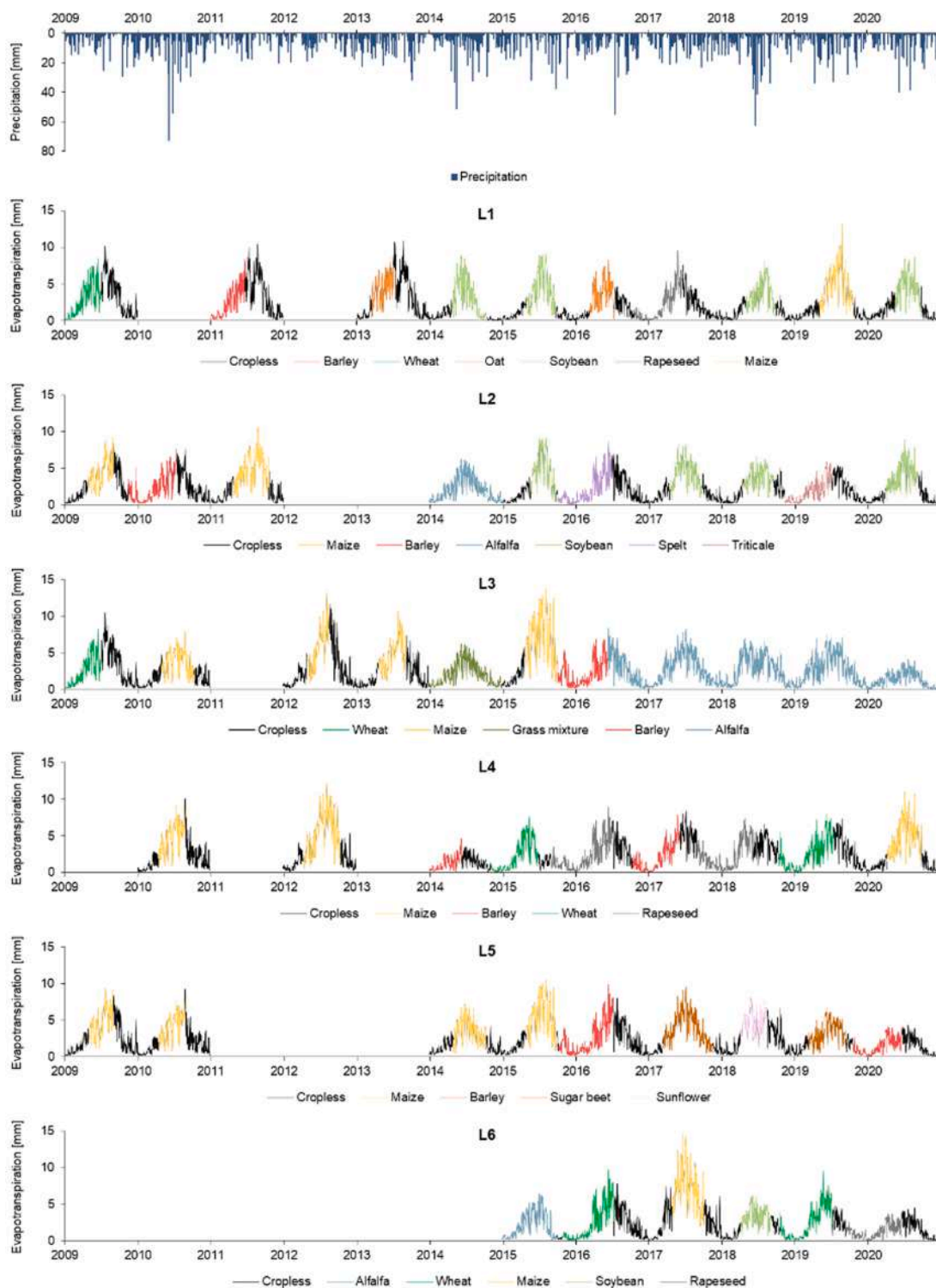


Fig. 5. Simulated evapotranspiration [mm] using HYDRUS 1D with daily precipitation [mm] during 2009–2020, at the investigated locations (L1 - L6). Black lines represent cropland simulations, while colored lines represent crop simulations.

leaching as well as fertilization costs without causing N deficiency in maize plants. Moreover, Rudnick and Irmak (2014) investigated the impact of the applied N rate on crop coefficients, and its decrease under irrigated and rainfed conditions. The variations in findings of outflow in the lysimeters (Fig. S4) at the investigated site can be linked to plant available water and N uptake, as water and N uptake increases with transpiration rates (Matsunami et al., 2010). The diversification of

planting crops presents different outcomes. Maize being the most frequent crop at the site had the highest average input and output of N in the investigated period. A higher ratio of input and output N, i.e., 16.6% for maize vs. 11.6% for the cereal group, implies a potential in adjusting the N management in the agricultural fields leading to economic and environmental benefits. Moreover, higher annual precipitation resulted in higher N output (Fig. S1).

3.3. Multivariate analysis

In the PCA carried out for the combined dataset, factor 1 explained 33.5% of the variance, while factors 2 and 3 explained 23.9% and 16.1%, respectively. Factor 1 had high negative loadings in the sand, bulk density and K_s , and high positive loadings in clay. Factor 2 had high negative loading in ET and high positive loading in precipitation and water outflow. Finally, factor 3 had high positive loading in nitrate outflow, N/IN, and N/out (Table 5). All dataset analysis identified three groups while intersected factors 1 and 2 (Fig. 6A) included: i) bulk density, sand fraction, and K_s ; ii) water outflow, nitrate outflow, N/out, N/in, and clay fraction; iii) ET. Groups i and ii were inversely related.

In the PCA calculated for cereal cropping, factor 1 explained 44.7% of the variance, while factors 2 and 3 explained 18.4% and 11.9%. Factor 1 had high negative loadings in precipitation, water outflow, nitrate outflow, and clay, and high negative loadings in ET, sand, and bulk density. Factor 2 had high positive loadings in K_s , while factor 3 had high negative loadings in N/in and N/out. The intersection of the factors 1 and 2 (Fig. 6B), identified two main inversely related groups: i) ET, sand, bulk density, and K_s ; ii) precipitation, water outflow, nitrate outflow, clay, and N/out.

In the PCA calculated for maize cropping, factor 1 explained 44.7% of the variance, while factors 2 and 3 explained 18.4% and 11.9%, respectively. At maize cropping two main inversely related groups (Fig. 6C): i) water outflow, precipitation, N/out, nitrate outflow, and clay; ii) sand, bulk density, K_s , and ET were identified. Moreover, multivariate analysis for maize cropping (Table 5) revealed high positive loadings in precipitation, water outflow, nitrate outflow, N/out, and clay, and high negative loadings in ET, sand, and bulk density at Factor 1. Factor 3 had high positive loading in N/in and K_s .

3.4. Nitrate concentration in relation to the depth

The highest (108.5 mg L^{-1}) concentration of nitrate was found at the shallowest depth (0.5 m) at L4, while all locations (except L6 - lysimeters installed in 2015) showed higher than 50 mg L^{-1} as maximum values (Fig. 7). From 2016 onward, at the same depth, concentrations did not exceed 30 mg L^{-1} . Moreover, all locations had a decreasing trend of nitrate concentrations over the investigation period. Previous investigations at the site concluded that groundwater levels have a decreasing trend, as well as this research shows (Fig. S4), while irregular precipitation events are present during the year that influence crop production (Mustać et al., 2020), which are likely linked to the nitrate concentrations at the site as well. A decreasing trend of nitrate concentrations was present with the depth of observation. The highest average concentrations (18.8 mg L^{-1}) of nitrate at a depth of 0.5 m were found at L4 (Fig. 7), along with the highest standard deviation (23.3 mg L^{-1}), while notably the low mean concentration (6.7 mg L^{-1}) was found at L6. Regarding the nitrate concentrations observed in soil-water at 4 m, concentrations were largely uniform, with higher

average values (4.4 mg L^{-1}) observed at L5. Furthermore, concentrations at 15 m are even lower, with the highest mean of 2.4 mg L^{-1} at L6. The high N concentration, mainly in nitrate and ammonium (Fig. S3), was accounted mostly in the plowing layers in which sophisticated responses have been exhibited concerning uptake, allocation, assimilation, and signaling (Hachiya and Sakakibara, 2017). It has to be pointed out that ammonium was also found in deeper monitoring wells (Fig. S3), which can also probably be linked to slower transformation rates or preferential transport of ammonium applied with fertilizers. It seems that nitrate decreased with depth faster than ammonium probably due to saturated conditions e.g., denitrification. The reaction has acquired and transferred the N for growth and productivity of the crop, possibly retarding its downward migration (Vidal et al., 2020). Besides, the aquifer loaded with high compressing soil has low permeability resulting in less leaching of nitrate. The compacted clayed soils are distributed dominantly with bimodal pore changing the fabric of the porous network and swelling the aggregate, hence bringing about the water retention properties (Romero et al., 2011). Additionally, due to the terminal steps of denitrification being distinct in diverse bacterial populations (Baker et al., 2015), needing oxygen as an energy supply that the deep layer lacks, the denitrification process mainly occurs in shallow water layers with less nitrate appearing in the deep layer.

3.5. Overall discussion and implications of nitrogen management in agricultural areas

The PCA analysis revealed different relations between soil properties and climate among three different procedures according to crops in rotation. Bulk density, sand fraction, and K_s were inversely related to water outflow, nitrate outflow, N/out, N/IN, and clay fraction for all dataset analyses. This is very similar to PCA analysis performed for cereal and maize cropping where both analysis groups consisting of bulk density, sand, K_s , and ET were inversely related to a group consisting of water outflow, precipitation, and nitrate outflow, N/out, and clay fraction. Other studies also found positive relationships between K_s and sand content and negative between K_s and clay content (Wesseling et al., 2009; Jarvis et al., 2013). Moreover, present research confirms that soil texture dominantly determines the retention characteristics in most agricultural soils. The bulk density increased with sand content, mainly due to the lack of micropores expressed in sandy soils (Koolen and Kuipers, 1984; Arvidsson, 1998). In addition, high compacted soils seem to mitigate leaching as is seen from negative interrelations between bulk density and water outflow, N outflow, and N/out. This process is visible under cereal, maize, and all other crops shown in Fig. 6. However, the relationships seem to be the highest expressed under maize cropping (Table 4) also indicating a poor plant canopy impact under maize on elevated leaching and loss of N.

Although investigated locations did not differ in tillage management and all farmers in study locations use conventional (plowing) tillage, we believe that transition to non-invertive or no-tillage could help to reduce

Table 5

Loading matrix with the first 3 factors extracted from the principal component analysis at the combined dataset and for cereal and maize crops. Eigenvalues retained in each factor are in bold.

Variable	All dataset			Cereal cropping			Maize cropping		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
Precipitation	0.602	0.562	-0.184	0.594	0.612	0.139	0.732	0.498	0.200
Water outflow	0.723	0.573	-0.165	0.733	0.583	-0.134	0.794	0.498	0.161
Nitrate outflow	0.595	0.334	0.545	0.687	0.137	0.292	0.681	0.052	-0.271
ET	-0.176	-0.663	0.399	-0.744	-0.241	0.301	-0.658	-0.404	0.222
N/in	0.330	-0.561	0.502	0.158	-0.464	0.669	0.064	-0.419	-0.587
N/out	0.718	0.059	0.634	0.499	0.087	0.819	0.845	-0.033	-0.191
Clay	0.649	-0.484	-0.203	0.625	-0.569	-0.103	0.812	-0.372	-0.109
Sand	-0.626	0.463	0.441	-0.748	0.373	0.407	-0.619	0.605	-0.008
Bulk density	-0.487	0.428	0.383	-0.556	0.445	0.230	-0.441	0.545	-0.280
K_s	-0.315	0.356	0.162	-0.258	0.592	-0.082	-0.303	0.295	-0.715

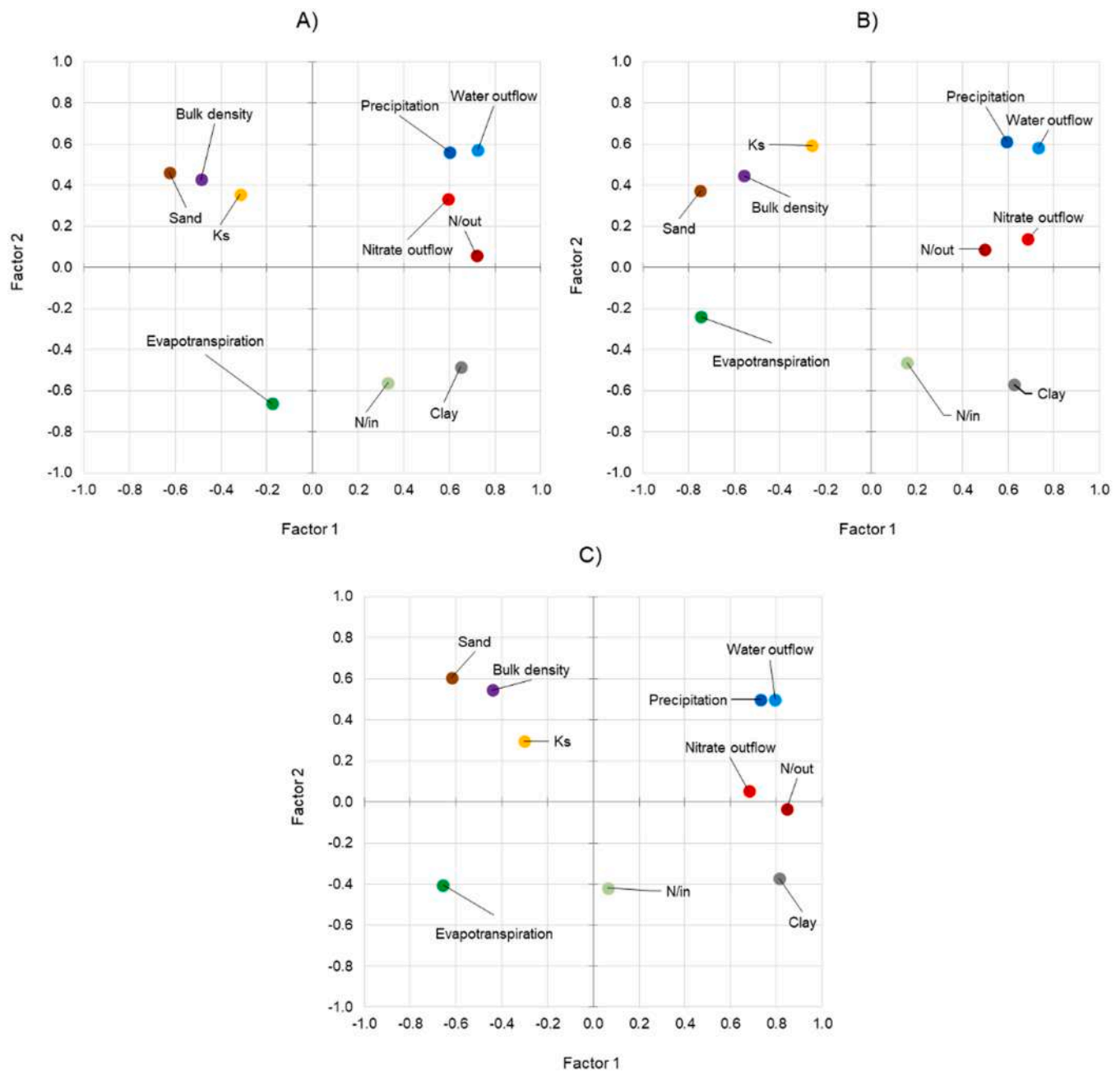


Fig. 6. Principal component analysis for the relation between Factors 1 and 2 for A) combined dataset, B) locations and years under cereal, and C) locations and years under maize cropping.

the N losses as is noted in other environments (Van Den Bossche et al., 2009; Xiao et al., 2019). Transition to conservation tillage improves the soil properties such as bulk density, soil penetration resistance, and soil particle size distribution (Wulannityas et al., 2021). Moreover, non-invertive tillage retains the residue on topsoil (Birkás et al., 2008) contributing to N leaching preservation. It is known that high-density crops and cover crops positively impact leaching and N loss (e.g., Beaudoin et al., 2005; Abdalla et al., 2019), and the long-term study presented in this paper also confirms these findings.

Cover crops and post-harvest residues, as sustainable agronomic practices, can serve as means of reducing nitrate losses by taking up water and nitrate from the soil after the main crop is harvested, and before the main crop begins to use significant amounts of water and N (Van Den Bossche et al., 2009; Shelton et al., 2018; Snapp and Surapur, 2018). Overall, the augmenting biomass of the covering crop can

suppress the growth of weeds, prevent nitrate leaching, and above-ground biomass N, and negatively affect the availability of inorganic N in the subsequent cropping season. Despite the increasingly important role the cover crops play, the drawback can be identified with the reducing grain yield of the primary crop, which can be avoided by choosing cover crops mixed with non-legumes and legumes (Abdalla et al., 2019). While the use of perennials in the cropping system helps in reducing nitrate leaching (Jungers et al., 2019), and even though there still is a challenge in increasing their adoption due to the problems of identifying profitable and marketable crops (Faber et al., 2012), there are promising perennial biomass crops that also hold multiple benefits for the agroecosystems and environment (Choi and Entenmann, 2019). In N management decision-making, understanding the relationship between N and crop rotation is of great importance due to several involvement points, such as the rate of N mineralization (Osterholz

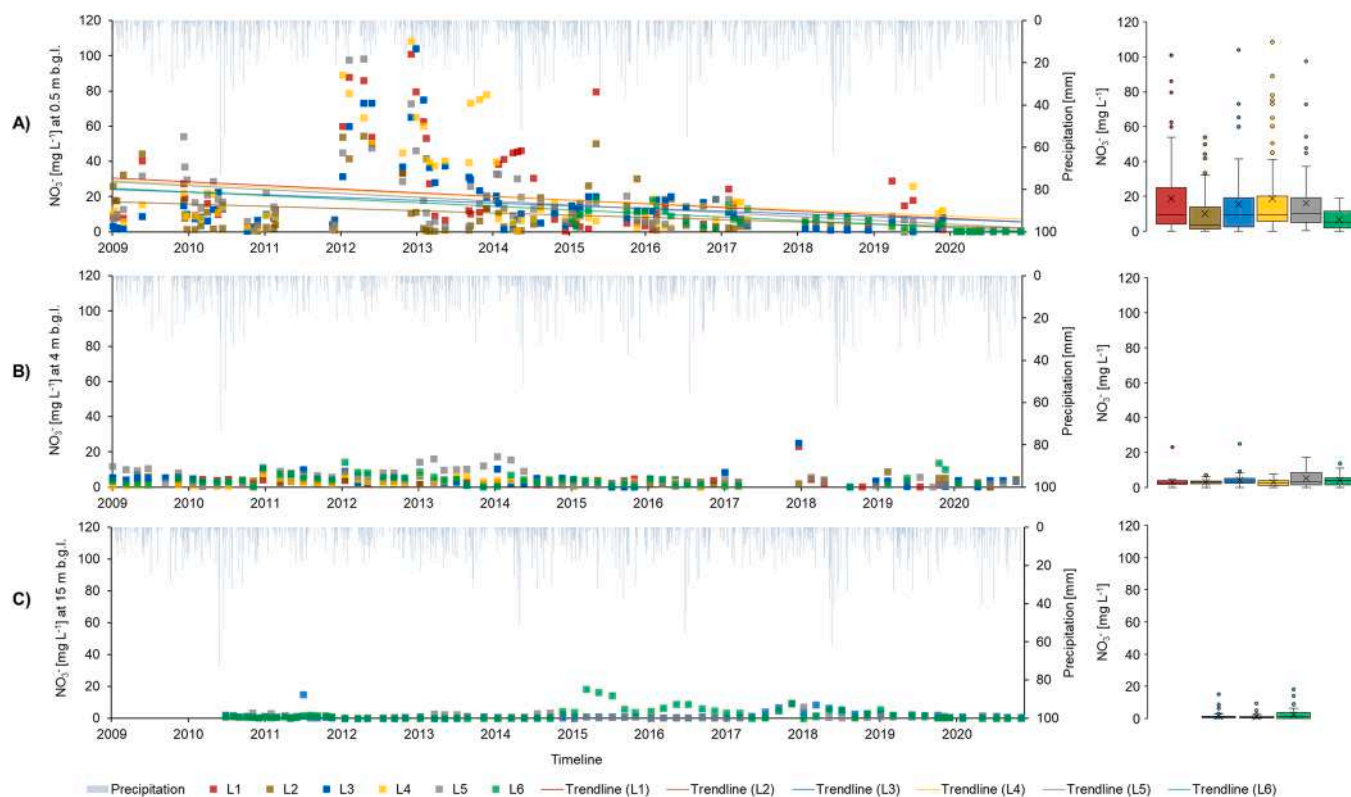


Fig. 7. Measured nitrate (NO_3^-) concentrations [mg L^{-1}] at A) 0.5, B) 4, and C) 15 m depths for soil-water sampling with daily precipitation [mm] during 2009–2020, at the investigated site (L1–L6), with boxplot representations of NO_3^- concentrations (whisker boundaries represent minimum and maximum values, lines represent median values, cross-marks represent mean values, dots represent outliers, and boxes represent the interquartile ranges).

et al., 2017) or the possibility of improved soil physical properties (Tueche and Hauser, 2011). Generally, crop rotation strategies have high crop yields than mono-cropping cultivation; in addition, the lesser N losses were discovered in a field planted with legumes (Miao et al., 2011). It is also noted that N mineralization, responding significantly to the N management, is a crucial process promoting N uptake by crops and increasing N loss potential. However, the rate of N loss during the mineralization can be brought down by immobilizing mechanisms, whose net N immobilization during immobilization-mineralization and immobilization is reduced through the change of plowing time and fertilizer application (Chen et al., 2014). Crop rotations preserve the soil quality by improving carbon, N, and microbial biomass in soil (McDaniel et al., 2014), and increasing crop rotational diversity also impacts positively the soil aggregation, organic carbon, total N, alleviating the reducing agroecosystems services (Tiemann et al., 2015).

N fertilizer applications for rate, timing, and method should be explored in each particular environmental condition, as their proper reduction and time of application could significantly reduce nitrate loss (Jeong and Bhattarai, 2018). Management practices like the type of tillage and time/number of fertilizer applications appear to be important factors for controlling the N uptake and losses. It is well known that conservation or reduced tillage practice supports the slower N mineralization and lowers the potential risk of nitrate leaching (Van Den Bossche et al., 2009). Others also noted higher N efficiency in conservation compared to conventional tillage systems (e.g. Pandey et al., 2010; Watts et al., 2010; Xiao et al., 2019). Moreover, the interactions between root-soil-microbial can stimulate soil N mineralization through rhizosphere priming effects raising the importance of fertilizing management affecting the crop's root functions (Zhu et al., 2014). Fertilizer management should be adjustable to environmental and plant conditions. However, it is a challenging task since fertilization usually increases gaseous N loss, N leaching, and plant yield (Shelton et al., 2018) – often a primary goal of farming.

4. Conclusions

The simulated water flow and nitrate loss fitted well with the collected data. The fitting was higher in years with higher precipitation which led to higher and more frequent lysimeter outflows thus resulting in more data points for model evaluation. The R^2 values for simulated water flow were 93% above 0.7, while R^2 values for nitrate simulations had lower values, being 73% above 0.7. The results of our research show that the use of the lysimeters data set in HYDRUS-1D can adequately address the water regime and nitrate dynamics in agricultural fields under long-term cultivation with diverse crops. The results of nitrate outflows in this study indicate that one-dimensional modeling, even though was found adequate, could possibly produce better data in two- (or three) dimensional simulations.

The leaching and accumulation of nitrate in the experimental site, relating to water outflow, were mainly affected by precipitation conditions, soil properties, and ET for all locations. The description of N was reflected well on the N uptake in an increasing trend in years with high transpiration rates; however, other main links in the field N cycle such as denitrification were underestimated and limitedly interpreted. The PCA capturing the connection of different soil parameters to N leaching characterized a negative correlation that combined 12 years' dataset. In exact cropping, the PCA highlighted other relationships between factor groups: for long-term planting of cereal and maize, the outflow of nitrate and N out were inversely related to ET, sand, bulk density, and K_s ; beyond that, the three factors independently reacted distinctively with variables. There is additional potential in adjusting the N management in agricultural fields to improve both economic and environmental outcomes, e.g. a higher output of N was found for maize (16.6%) than the cereal group (11.6%).

All locations (L1–L6) had a decreasing trend of nitrate concentrations over the investigation period. The research highlights the importance of exploring N fertilizer application in each particular environmental

condition, as proper reduction and time of application reduces nitrate loss. The results indicate that using tools such as agro-hydrological models may improve opportunities to ameliorate N management in agricultural fields in the future. This information is critical to fine-tuning N management in agricultural watersheds, leading to improved N use efficiency, lower N losses, and protection of water quality in sensitive water bodies.

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.

Data Availability

Data will be made available on request.

Acknowledgment

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.agwat.2022.108039](https://doi.org/10.1016/j.agwat.2022.108039).

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