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Denitrification in the vadose zone: Modelling with percolating water prognosis and denitrification potential

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ABSTRACT

Transport and transformation processes of nitrogen in the soil are an essential part of understanding the relationship between agricultural input and nitrate (NO_3^-) concentrations in groundwater. The presented study describes these transformation processes around NO_3^- degradation at a water catchment in the Lower Rhine Embayment, Germany. Despite intensive agriculture, extracted groundwater at a depth of 21 to 22 m shows unexpectedly very low NO_3^- levels, below 3 mg/L NO_3^- for all wells. The local water supplier therefore carried out investigations in this area and generated soil data from 22 representative areas (142 soil samples from 82 drilling meters from the surface to a max. depth of 5.5 m) and groundwater analyses from 17 groundwater monitoring wells (from 3 to 5 m below ground surface). Soil types are predominantly luvisol and gleysol. The substrate in the topsoil is mainly clayey silt; underneath there are mostly medium-grained sands with partial silt intercalations which appear as a separate layer. Based on this dataset, the percolating water residence times and the NO_3^- leaching potential were calculated in this study. Together with the nitrogen surplus and with the help of reactive transport modelling, the denitrification potential in the vadose zone was simulated. The comparison of simulation results with laboratory-measured data shows a high correlation. Substantial NO_3^- reduction in the vadose zone was observed: dependent on soil type, reduction capacity and water residence time, up to 25% of the NO_3^- was reduced here. The applied modelling is considered an improvement in NO_3^- degradation potential assessment because it considers many relevant variables such as precipitation, soil parameters (grain size, field capacity, available water capacity, coarse fragments) and nitrogen input. Therefore, a transfer to other sites with comparable hydro(*geo*)logical conditions is possible, also due to relatively easily determinable input data. This assessment of nitrogen degradation in the vadose zone will be a useful tool for NO_3^- levels forecast in groundwater

1. Introduction

Most of the nitrogen (N) input to soils and groundwater is caused by agricultural fertilization. The respective N demand for crop growth is based on land use. To develop suitable and sustainable countermeasures to excess N migration from soils to groundwater, it is essential to characterize and forecast its fate from fertilization to groundwater entry, including passage through the vadose zone. Prediction of N input and discharge via the unsaturated soil zone into groundwater was investigated in many studies (e.g. Aulakh et al., 1992; Stenger et al., 2002; Baran et al., 2007) with the majority of current research examining the rooted soil zone and its potential for nitrate (NO_3^-) reduction. To better predict how much NO_3^- reaches the groundwater zone in a given time span, the main denitrification processes (chemo-organotrophic and chemo-lithothrophic denitrification) need to be taken into account. In these processes, NO_3^- is converted under mostly anaerobic conditions by

Abbreviations: A%, Exchange Frequency; A_{RD}, depth of root horizon; A_{pl}, soil water available; A_{pot}, potential leaching of nitrogen in soil; A_{rh}, depth of root horizon leaching; D_{max}, max. denitrification rate; d_{soil}, denitrification loss in the soil; Fc, Field Capacity; FcRD, Field Capacity in the effective root zone; GWR, groundwater recharge; k, Michaelis constant; NG, Nitrogen discharge after the denitrification; N_{min}, autumn available mineralized; N_{mint}, depth of N_{min} sample; N_{minN}, measured, excess nitrogen; N_{su}, summer precipitation; N_{Wi}, winter precipitation; N(t), NO_3^- level after the residence time; PV, percolation velocity; pw, NO_3^- concentration in percolating water; t, residence time; t_{soil}, residence time of the percolating water; ufc, usable Field Capacity; ufcRD, soil water available to plants crop rooting depth.

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reducing agents (organic carbon or sulphide-S) with the help of denitrificants (microorganisms). Nitrate is converted into nitrite, nitric oxide, nitrous oxide, and molecular nitrogen. The major process is the reduction of NO_3^- to N_2 gas in a metabolic oxidation of organic matter (Canfield et al., 2010), which is a main pathway for reactive N removal. This study investigates the unsaturated zone below the root horizon (in the following referred to as deep vadose zone) in an area affected by intensive agricultural use. The water retention time combined with the NO_3^- input into this zone and subsequent reduction, allow a quantitative conclusion on the degradation efficiency of the deep vadose zone. Numerous studies have investigated the leaching of NO_3^- into the deep vadose zone below the root zone (e.g., Seong and Rubin, 1999; Onsoy et al., 2005; Fraters et al., 2006; Botros et al., 2012; Turkeltaub et al., 2016; Baram et al., 2017; Turkeltaub et al., 2018). Most assume no denitrification or a negligible amount in this area (Schulte-Kellinghaus, 1988; Chen et al., 2018). To the authors' best knowledge, no approach combining N input, water retention time and discharge has been presented so far to predict N fate in the deep vadose zone. Knoll et al. (2020) estimate NO_3^- reduction across the unsaturated zone and the groundwater body. They combine different aspects of the flow paths of nitrate-N through the vadose zone and groundwater but for simplification, they assumed NO_3^- for the entire N load in the percolating water, and no reduction between the root zone and the groundwater. Individual ex situ experiments to determine the denitrification potential provide information on individual situations. The difficulty is the upscaling to real conditions. We consider a unified, simple model which approximates the discharge of N in different soil zones more useful to predict N flow because it can determine NO_3^- input into the aquifer relatively quickly and allows for an estimation of the denitrification potential of the deep vadose zone in a given area. The complex situation in the soil zone due to different hydrogeochemical conditions and processes makes a general model difficult. A mass balance study by Onsoy et al. (2005) using 1200 soil samples showed the heterogeneity and complexity in the deep vadose zone. Denitrification depends on various factors such as oxygen concentration, carbon concentration, pH, temperature, percolating water residence time, N input and types of microbes (Rivett et al., 2008). In addition, studies such as He et al. (2018) show that climate change is likely to have an impact on NO_3^- leaching from the vadose zone in the future. Nitrogen can accumulate in the soil over a longer time span during dry periods and then be increasingly washed out in the form of NO_3^-. Studies suggest that there may be a large increase in NO_3^- concentrations in groundwater in some regions of the earth in the future. Due to lower groundwater recharge, NO_3^- concentrations increase as a result of missing dilution (Ducharne et al., 2007; Ortmeyer et al., 2021).

Due to this fact it is even more important to understand relevant hydrogeochemical processes in the unsaturated zone. Furthermore, NO_3^- storage in the vadose zone can be much higher than often expected. Ascott et al. (2016) estimate a potential high impact in areas with a thick vadose zone and extensive historical agriculture. The percolating water has a longer travel time that leads to a delay that will have an impact on groundwater quality. In this study, an agricultural area in the Lower Rhine Embayment, western Germany, is investigated. A local water supplier carried out investigations in this area and collected data consisting of soil and groundwater analyses which were used as the database. Despite high N inputs, groundwater shows low NO_3 concentrations. The hypothesis is that the discrepancy between the mass of N input and the mass of N discharge into the aquifer is caused by NO_3^- reduction in the unsaturated zone. This deep vadose zone below the root zone is therefore the presumed decisive factor for the reduced NO_3^- input (up to 25%). The aim of this work is to develop and test a model which allows an estimation of the denitrification potential below the root zone with easily available variables such as precipitation, soil parameters and N input. This is achieved by modelling using Michaelis-Menten kinetics. This approach combines the kinetics of 1st and 0th order depending on NO_3^- concentration in the percolating water and is coupled to the water residence time (Bowman and Focht, 1974).

The model helps estimate the entry of NO_3^- via percolating water into the aquifer over a larger area. The predicted NO_3^- reduction allows conclusions to be drawn about the expectable concentration in groundwater. Effective groundwater pollution from agriculture can thus be better predicted. In addition, the deep vadose zone is illuminated regarding its capacity for NO_3^- reduction.

2. Materials and methods

2.1. Site description

The area is located in the Lower Rhine Embayment in the western part of the German federal state North Rhine-Westphalia, about 10 km from the city of Mönchengladbach. Geologically, the Embayment is an intraplate rift structure within the European Variscan Mountains, active since Paleogene times and filled with a thick succession of Oligocene to Quaternary sediments representing a multi-aquifer formation. In the study area, highly permeable fluvial Quaternary sediments (terraces of the river Rhine) contain substantial groundwater resources used for drinking water production. The about 30 m thick sands and fine gravels partly overlie the Paleogene as one aquifer, while in other parts two aquifers developed, separated by an interglacial aquitard (Grabert, 1998).

In the studied water catchment, groundwater is extracted from the bottom of the Quaternary sediments. In the forested northern part, depth to groundwater table is between 1 and 3 m below ground surface while in the southern agricultural areas, it is between 3 and 5 m below ground surface. The average water-table depth for soil drilling sites is 3.43 m. Pedologically (using the classification after IUSS Working Group WRB, 2015), most of the investigated agricultural land in the southern part of the study area can be assigned to the type luvisol. In the northern part, there are mainly semi-terrestrial soils with groundwater-influenced soil types gleysol and stagnosol. In the northeastern forested area, lowland moor soils are common along the stream. The semi-terrestrial soils can partially migrate bioavailable organic matter into the unsaturated zone (Mehranfar, 2003). The northern part is therefore predestined for chemo-organotrophic denitrification. Most of the arable land can be classified as gleyic luvisol (Fig. 1).

In terms of groundwater NO_3^- concentrations, a decreasing trend from south to north can be observed. Concentrations above the drinking water limit are regularly measured in the southernmost part (not completely shown in Fig. 1). The German Drinking Water Ordinance stipulates a maximum value for NO_3^- of 50 mg/L (TrinkwV 2001). In the following, all presented nitrate concentrations in mg/L are expressed as NO_3, not as NO_3-N. The production wells are in the northern part, where NO_3^- levels are very low (Fig. 1), or groundwater is virtually NO_3^--free. The annual average NO_3^- concentration of 17 groundwater monitoring wells in the last decade is between about 13 and 23 mg/L (Fig. 2). The average sampling depth of the groundwater samples is 5.5 m, the maximum is at 10 m. Furthermore, the monitoring stations in the water catchment have shown almost constant levels of Cl^- (average 41 mg/L with a max. 23% deviation), SO_4^{2-} (average 113 mg/L with a max. 20% deviation) and HCO_3^- (average 379 mg/L with a max. 6% deviation) concentrations during the last decade.

2.2. Vadose zone sampling

In the investigation area, soil samples were obtained from deep drillings as ram core samples from 22 locations. These are divided into 19 arable areas, 1 grassland area (no. 24) and 2 forest areas (no. 25 and 26) (Fig. 1). The soil between 1 m below ground level and the groundwater surface (and partly beyond the latter) was explored. The deep vadose zone was recorded, which extends from underneath the root zone to the groundwater. The soil samples are taken layer by layer in depth sections of 50 cm thickness each. The root horizon was fixed (defined by the soil mapping guide (Ad-Hoc-AG Boden, 2005) at 1.1 m because of

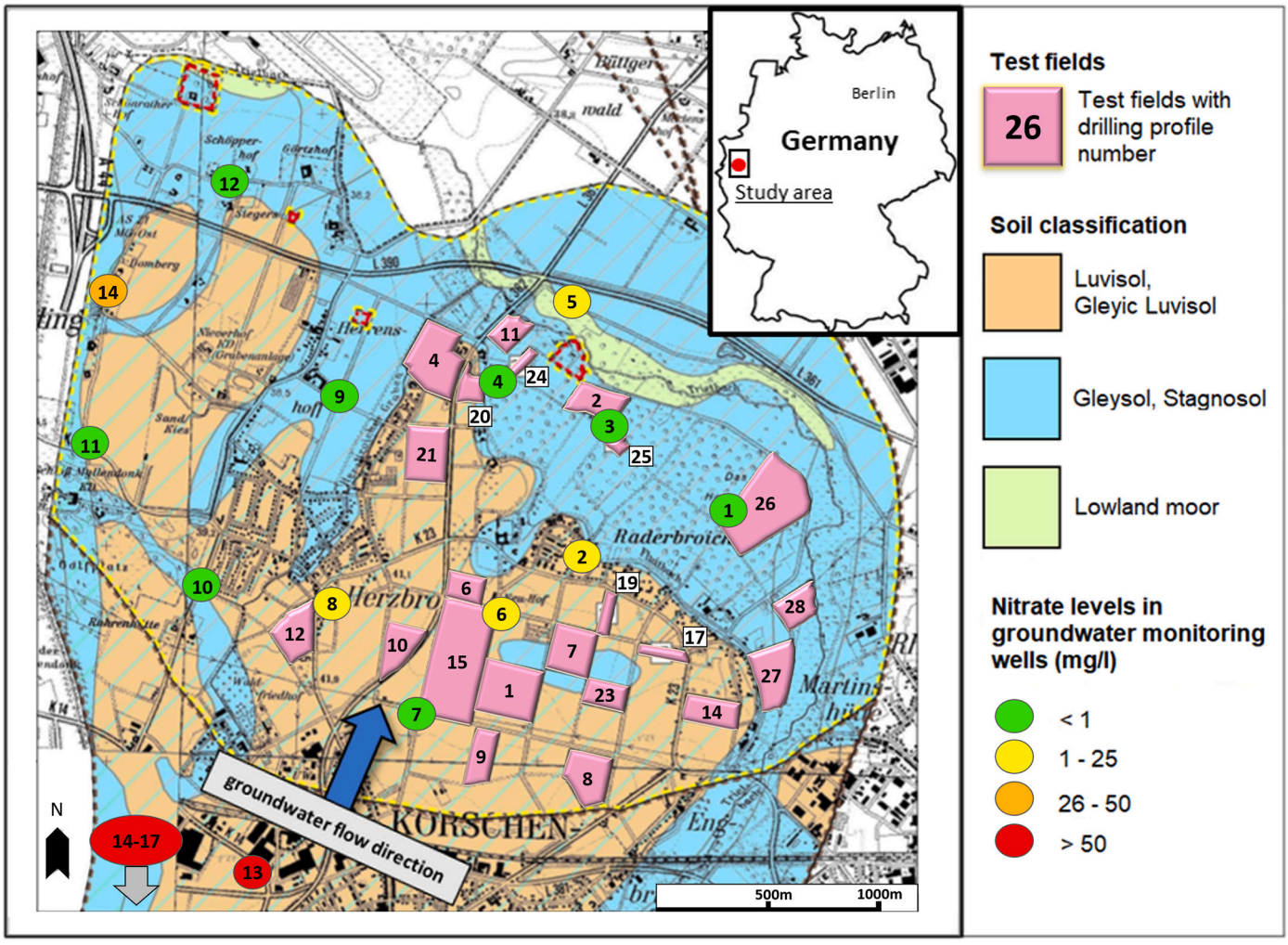


Fig. 1. Study area with test fields (including soil drilling profile labels), soil types and groundwater NO_3^- levels. The map shows the water protection zones with dashed lines (red: zone 1; yellow: zone 2; brown: zone 3). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the root penetration depth in the given soil types. For the determination of NO_3^-, photometric determination was carried out by a continuous flow method (Continuous-Flow Analysis, Flow Injection Analysis, SFA) with dialyzer and Cd/Cu reduction column. This is a standard procedure according to DIN 38406-E5 (VDLUFA method Volume I A 6.1.4.1.). Calibration is carried out with a series of NO_3^- standard. 25.0 g of dried sample is mixed with 100 ml of an extraction solution of 0.0125 M calcium chloride solution. The suspension is shaken with an overhead shaker for 30 min at approx. 30 rpm. The analyses were carried out by a certified analytical laboratory (Wasserlabor Niederrhein GmbH). Concentrations of NO_3^-, SO_4^{2-} and NH_4^+ were quantified. Additionally, the soil was analyzed (soil substrate, humus content, color, carbonate content, moisture, hydromorphic characteristics) according to Ad-Hoc-AG Boden (2005). The soil types described here have been transferred to the WRB classification (WRB, 2015). This is important for determining the soil type and the soil conditions. A total of 142 soil samples were taken.

2.3. Modelling framework

To estimate the denitrification potential in the vadose zone, the "DENUZ" (Denitrification in the unsaturated zone, German abbreviation) model (Wendland, 2010) is used as a basis for an approach that considers the upper soil type and environmental parameters. Therefore, different initial data such as soil parameters, precipitation and empirical data are necessary. The required values are calculated or determined by values based on empirical studies. The equation is:

$$N(t)\frac{dN(t)}{dt} + D_{max} * \frac{N(t)}{k + N(t)} = 0 \quad (1)$$

where N(t) is the NO_3^- level after the residence time [kg N/(ha*a)], t is the residence time [a], D_{max} is the max. denitrification rate [kg N/(ha*a)], k is the Michaelis constant [kg N/(ha*a)].

It has been shown that the soil type reflects the most important influencing factors like soil water content, availability of organic carbon, temperature and pH (NLKWN, 2010). In the DENUZ model, soil types are divided into classes of denitrification rates. Maximum values (D_{max}) for denitrification of the individual soil types were determined. The calculation details are provided in the next subsection.

To model time-dependent denitrification, the DENUZ model uses the Michaelis-Menten kinetics, following the example of Bowman and Focht (1974). This describes the relationship between enzymatic reaction rate and substrate concentration. The constant k influences the range in which the NO_3^- conversion is controlled by the NO_3^- concentration.

The time is represented by the residence time of the percolating water (t). The dissolved N in the percolating water moves gravimetrically via precipitation towards groundwater. The residual N in the soil is used as the initial value (autumn available mineralized nitrogen =

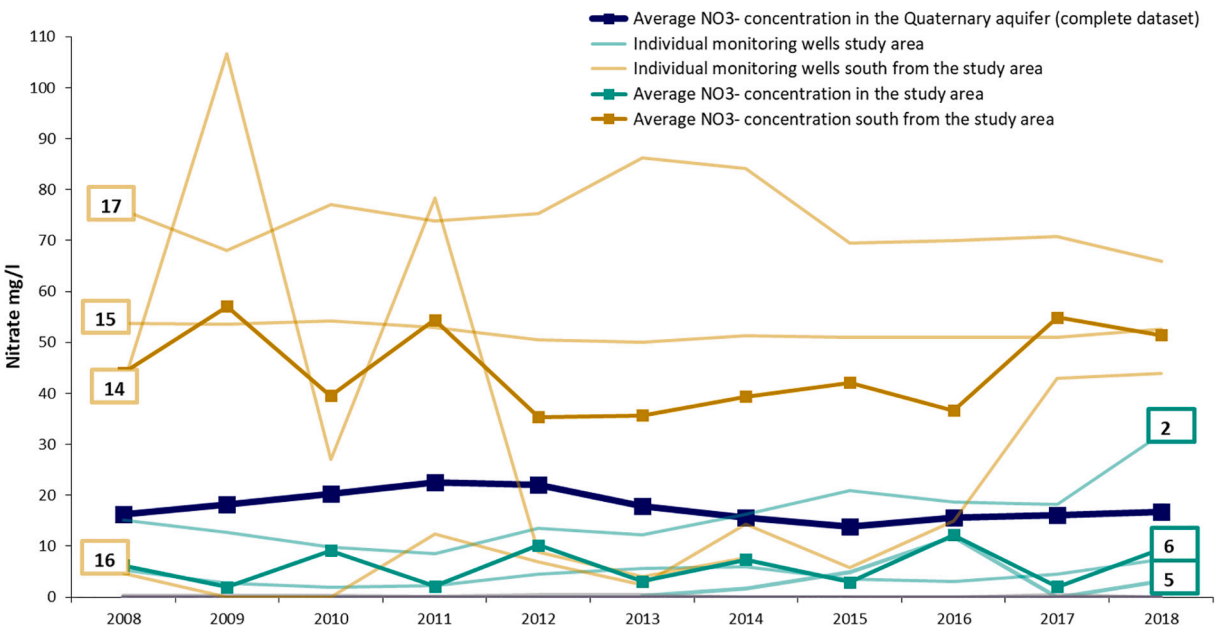


Fig. 2. Average NO_3^- concentration in groundwater development for 17 groundwater monitoring wells in the Quaternary aquifer (analyzed by NEW Niederrhein GmbH during groundwater monitoring). 8 wells show NO_3^- below the analytical detection limits (<0.1 mg/L), or very low concentrations (<5 mg/L). Numbers in squares indicate monitoring well IDs, cf. Fig. 1.

N_{min}). This value is measured around mid-November, as this is usually the time when percolating water begins to form in substantial volumes. It is assumed that the N is mobile in the form of NO_3^- in the topsoil. Fig. 3 gives an overview of the calculation approach.

Field capacities and groundwater recharge are calculated and used to estimate the percolating water residence time. The soil type determines the maximum denitrification rate and the constant k. The autumn N_{min} value provides the initial concentration of N that is potentially washed out into the deep vadose zone. Using the Michaelis-Menten equation, denitrification is calculated as a function of residence time, soil type and excess N (Fig. 3).

2.4. Percolating water residence time

The method after Renger (2002) is used to determine the NO_3^- shifting depth and duration of stay. Firstly, the amount of percolating water is calculated. The percolating water flows vertically into the groundwater without any intermediate flow. Eqs. (2)–(4), calculating groundwater recharge, show that the influencing factors are winter (N_{Wi}) and summer precipitation (N_{Su}), evapotranspiration according to

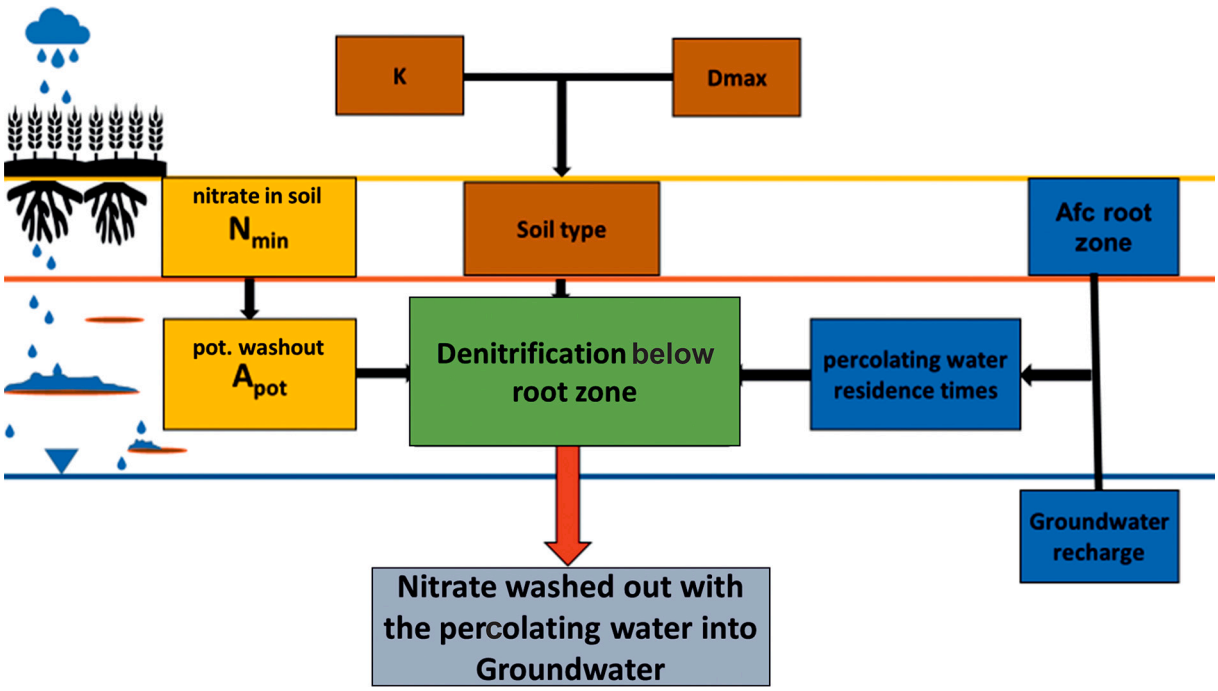


Fig. 3. Components of the modulation in the different zones used to estimate denitrification (k is the Michaelis constant, D_{max} is the max. denitrification rate, N_{min} is autumn available mineralized N, Afc is available field capacity, A_{pot} is potential leaching of N from soil).

Haude (1954, E_{HAUDE}) and the amount of soil water available to plants (A_{pl}).

Arable land

$$v = 0,92\ (N_{wi}) + 0,61\ (N_{Su}) – 153\ (log\ A_{pl}) – 0.12\ (E_{Haude}) + 109 \quad (2)$$

Grassland

$$v = 0,9\ (N_{wi}) + 0,52\ (N_{Su}) – 286\ (log\ A_{pl}) – 0.10\ (E_{Haude}) + 330 \quad (3)$$

Coniferous forest

$$v = 0,71\ (N_{wi}) + 0,67\ (N_{Su}) – 166\ (log\ A_{pl}) – 0.19\ (E_{Haude}) + 127 \quad (4)$$

A nearby weather station 5 km away, provides the amount of precipitation and potential evapotranspiration after Haude. The groundwater recharge is attributed to corrections due to cultivation since the equation for arable land is based on winter wheat as a standardized crop. The usable field capacity of the crop rooting depth ufc_{RD} is calculated by multiplying the individual usable field capacities of the soil types by the effective root zone thickness:

$$ufc_{RD}\ (mm) = ufc\ \left(\frac{mm}{dm}\right) * crop\ rooting\ depth\ (dm) \quad (5)$$

The crop rooting depth [RD] is fixed at a depth of 11 dm for gleysol and stagnosol. The ufc_{RD} is a measure for soil water available to plants. The field capacity is determined analogously. A mean storage density of 1.55–1.8 g/m^3 is defined by the soil mapping guide (Ad-Hoc-AG Boden, 2005). For further classification, the storage density is assigned to dry bulk densities [pt]. Based on the dry bulk densities combined with the individual soil types, the usable field capacity can be determined. The proportion of organic matter and the proportion of coarse soil must be considered in the calculation. For this purpose, the humus content is converted into organic matter content (Table 1).

The coarse soil content is to be considered because larger skeletal components in the soil have a negative effect on the field capacity. The average coarse soil content is 18% (SD = 22.29). It differs for each test field from 0% to 68% due to high variability. The residence time is calculated from the deep infiltration quantity and the field capacity under the root zone. The field capacity is used because there is no influence by plant roots in this zone:

$$t_{soil} = \frac{FC * d}{PV} \quad (6)$$

where t_{soil} is the residence time of the percolating water [a], PV is the percolation velocity [mm/a], FC is the field capacity [mm/dm], d is the layer thickness of the zone [dm].

An average value is calculated for the field capacity of the zone for each area. This represents the averaged field capacity of the individual soil layers per field profile. It is multiplied by the layer thickness of the deep vadose zone and divided by the amount of percolating water (Eq. (6)).

2.5. Nitrogen input and leaching

It has been shown that an accurate estimation is achieved with the help of N-demand determination patterns. It is an alternative representation of surplus NO_3^- at the end of the growing season (Carey et al., 2017). Determining the real N surplus is difficult due to various factors.

Table 1
Statistics for soil properties (topsoil): total C_{org} content (wt.-%), humus content (wt.-%), total N content (wt.-%), C/N ratio.

	Total C (org) %	Humus content %	Total N %	C/N ratio
average	1.25	2.2	0.12	11
max	1.62	2.8	0.16	12
min	0.93	1.6	0.09	10

The heterogeneity of the different sites and their different management allow wide ranges of N surpluses.

The measured autumn N_{min} content in the soil provides information on the amount of N in the soil. This value represents the available soil N, which can potentially leach out with the percolating water. The autumn N_{min} value is influenced by various factors, the most important of which are crop type, harvesting technique and the mineralization potential of the soil (Sullivan and Cogger, 2003). It is measured shortly before the formation of percolating water due to high autumn precipitation. The relationship between N-balance, N_{min} and NO_3^- concentration in the leachate is described in Bechtel (2008). Other studies use the N_{min} to estimate the soil net N on a larger scale (Risch et al., 2019).

Several authors were able to estimate NO_3^- discharge by using autumn N_{min} (Scheffer, 1999; Bechtel, 2008). In this study, the average autumn N_{min} is derived from the calculation of 21 arable land areas. These are from the cultivation years 2016 to 2018, with average N_{min} values of 85 kg N/(ha*a) potential NO_3^- discharge.

The amount of N leached into the deep vadose zone depends on the exchange frequency EF. The higher the frequency EF, the more NO_3^- can potentially be washed out. To determine the potentially leachable excess N, Eqs. (7) to (9) are used (NLWKN, 2010). The leachable excess N consists of the individual N species NO_3^-, NO_2^-, NH_4^+, NH_3 and NH_4^+. Eq. (7) describes the percentage of soil water that is exchanged within one year. The simplified case of uniform downward displacement of water is assumed. Values above 100% represent a complete exchange of the soil water, the exchange frequency (EF) is 1. For values below 100%, the respective value corresponds to the percentage washout A%. The calculation is based on the published recommendations of the Lower Saxony State Office for Water Management, Coastal and Nature Conservation (NLWKN, 2010). These are calculated according to:

$$EF = \left(\frac{GWR}{FC_{RD}}\right) * 100 \quad (7)$$

where EF is the exchange frequency of soil water [%], GWR is the groundwater recharge [mm/a], FC_{RD} is the field capacity in the rooted soil [mm]. $A_{\%}$ is EF/100 if EF < 100 and EF = 1 if EF > 100.

If the sample depth does not correspond to the depth of the root horizon, the exchange frequency must be adjusted in percentage to the depth (8). Based on the sample depth of the N_{min} data, the leaching of the measured N_{min} value of the soil is calculated as a percentage:

$$A_{rh} = A_{\%} * RD \quad (8)$$

where A_{rh} is the depth of root horizon leaching [m], A% is the exchange percentage [−], RD is the root horizon thickness [m]. The potential leaching is then calculated by multiplying the depth of leaching of the root horizon by the depth of N_{min} sampling multiplied by the measured N_{min}:

$$A_{pot} = \frac{A_{RD}}{Nmin_t} * Nmin_N \quad (9)$$

where A_{pot} is the potential soil N leaching [kg N/(ha)], A_{RD} is the depth of root horizon leaching [m], N_{mint} is the depth of N_{min} sample [m], N_{minN} is the measured excess N [kg N/ha].

It is assumed that the NH_4^+-N content is of minor importance (NLWKN, 2010). To predict the NO_3^- concentration in the percolating water, the autumn N_{min} value is converted according to:

$$pw = \frac{A_{pot} * 443}{GWR} \quad (10)$$

where pw is the NO_3^- concentration in the percolating water [mg/L], A_{pot} is the potential leaching of N from the soil [kg N/ha], GWR is the groundwater recharge [mm/a], 443 is the conversion factor (4.43) of NO_3^- with the factor 100 [−].

2.6. Estimating denitrification potential

The degradation capacity of the zone below the root zone is based on the classification of the maximum potentials of the soil according to NLKWN (2010). For the calculation, the deep vadose zone under the soil type gleyic luvisol is set to a maximum denitrification capacity D_{max} of 10 kg N/(ha*a). The zones below gleysol and stagnosol were set to a D_{max} of 30 kg N/(ha*a). At these sites, new organic matter can be introduced into the vadose zone leading to anaerobic NO_3^--reducing conditions. Therefore, the potential for denitrification is substantially increased. Evaluation of the denitrification potential of individual soil types is taken from Müller and Raissi (2002). The classifications are each at the lower limit of the classes, such that the potential is estimated rather conservatively.

2.7. Model parameterization

The DENUZ model approach assigns a pair of D_{max} and k values to each denitrification level. According to Köhne and Wendland (1992), the constant k is set to values between 18.7 kg N/(ha*a) (good denitrification conditions) and 2.5 kg N/(ha*a) (poor denitrification conditions). In this study, the constant k is set to 2.5 kg N/(ha*a) at a D_{max} of 10 kg N/(ha*a) and to 4 kg N/(ha*a) at a D_{max} of 30 kg N/(ha*a) (Köhne and Wendland, 1992).

The percentage of denitrification loss is given by:

$$d_{soil} = \frac{N(t)}{N0} * 100 \quad (11)$$

where d_{soil} is the denitrification loss in the soil [−], N(t) is the N content in the soil after the percolation time t [kg N/(ha*a)], N0 is the N content in the soil [kg N/(ha*a)] that is equivalent to N_{min}.

N(t) is solved iteratively according to Eq. (1). Thus, the reduction over time is simulated.

The N discharge from the vadose zone is calculated by

$$N_G = N0 - N(t) \quad (12)$$

where N_G is the N discharge after the denitrification [kg N/(ha*a)], N(t) is the N content in the soil after the percolation time t [kg N/(ha*a)], N0 is the N discharge in the soil [kg N/(ha*a)].

3. Results

3.1. Processes in the vadose zone

Hydromorphic soil characteristics may give an indication of reduced conditions. These occur in almost all profiles as bleached or marked green-grey to blue-grey colors. Fig. 4a and b show the decrease of NO_3^- concentrations in soil solutions towards depth with a constantly low SO_4^{2-} concentration in the leachate.

Fig. 4a shows a profile of land section 6 (cf. Fig. 1), on which summer wheat and turnips were cultivated from 2016 to 2018. On land section 27 (Fig. 4b, cf. Fig. 1), a crop sequence of wheat-arable grass-maize was cultivated in the same period. The soil type in land section 6 can be assigned as gleyic luvisol and in land section 27 as gleysol.

3.2. Nitrogen input

For the N discharge, the average of all profiles from autumn N_{min} is considered. The rooting depth is 1.1 m. A calculated average groundwater recharge of 202 mm/a is used. The average field capacity for all

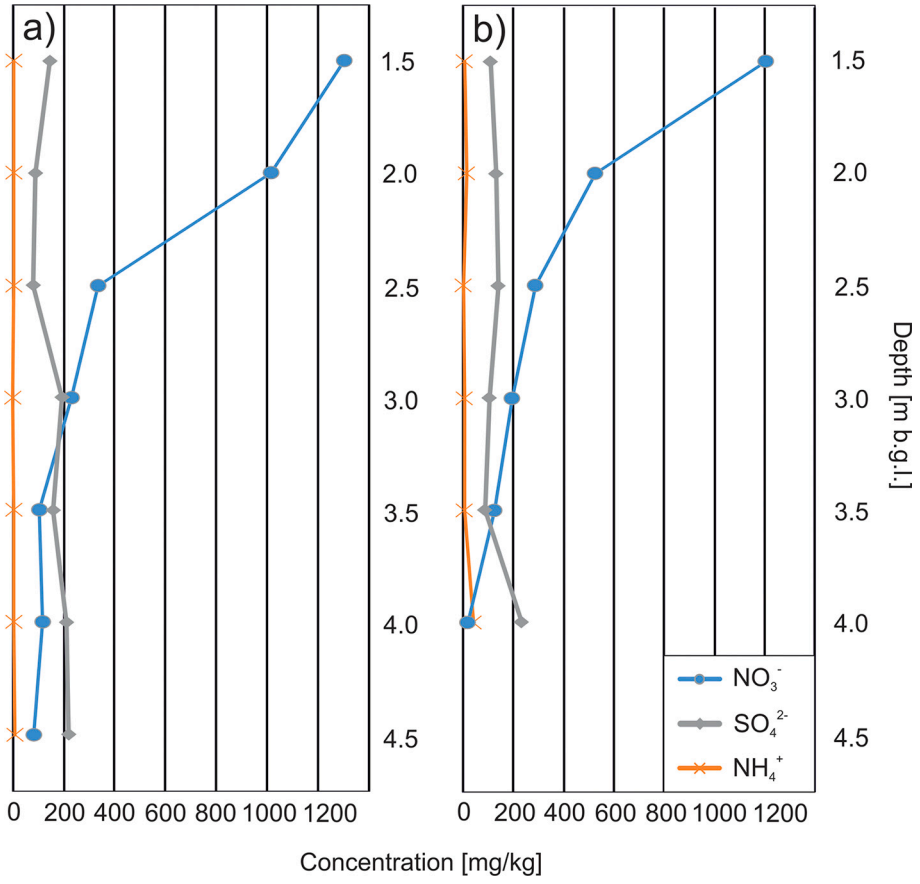


Fig. 4. Exemplary depth profiles: NO_3^-, SO_4^{2-} and NH_4^+ concentration in percolating water from the extraction of soil samples with CaCl-solution a) section 6; b) section 27.

areas is 365 mm (Table 2).

Annually, an average of 57 kg N/ha (NO_3^- and NH_4^+ combined) is washed into the deep vadose zone that begins in a depth of 70 bis 110 cm below the surface.

3.3. Relative denitrification

The input value is 57 kg N/(ha*a). The different denitrification rates in the zones are shown in Fig. 5. While the vadose zone at the gleysol/stagnosol sites has denitrified 90% of the N after a percolating water residence time of almost two years, the zone at the gleyic luvisol sites requires more than five years for the same percentage.

The average retention time of the percolating water under the gleyic luvisol soil is 2 years, that of the stagnosol/gley 1.8 years (Table 1). This corresponds to an average reduction of 34% of the input N in the deep vadose zone at the gleyic luvisol sites while for the other sites, average reduction is 63%. Consequently, at the gleyic luvisol sites, an average of 37.7 kg N/(ha*a) remains as residual N which can potentially be introduced into groundwater with the percolating water. At the stagnosol sites, 23.4 kg N/(ha*a) remain. This corresponds to a residual amount of 41% to 66% of the originally calculated input N. The potential of denitrification below the root zone has been calculated individually for each arable site. To make a general comparison, the average of the last half meter before groundwater is used. This average NO_3^- concentration is 85 mg/L. The calculated value for an average excess after denitrification is 35 kg N(ha*a), which corresponds to a NO_3^- concentration of 79 mg/L. The deviation of the NO_3^- concentrations of the calculated values to the measured ones is therefore only 6 mg/L (or about 7%).

In Fig. 6, the concentration curve of NO_3^- is shown as an average development of all arable sites with depth. At a depth of 4 m, the average measured concentration is 90 mg/L. 11 profiles go down to a depth of 4 m, which still allows for a good comparison. Overall, measured concentrations decrease from 121 mg/L to 90 mg/L. This corresponds to a decrease of 31 mg/L over 3 m thickness (or converted to the N input: 14 kg N(ha*a) using a percolating water quantity of 202 mm/a).

Table 2
Calculated parameters for soils in the different profiles (Pwr: percolation water residence time, uFcr: usable field capacity root zone, Fc: field capacity, Prc: percolation rate for cropland).

Profile #	Pwr	uFcr	Fc	Prc	Soil type
	a	mm/dm	mm/dm	mm/a	
1	1.68	218	326	227	gleyic luvisol
2	1.30	245	369	191	gleyic luvisol
4	2.17	216	406	200	gleyic luvisol
6	1.58	222	360	204	gleyic luvisol
7	3.79	266	403	186	stagnosol
8	3.24	206	313	203	gleyic luvisol
9	2.14	193	287	217	gleyic luvisol
10	1.29	183	288	217	gleyic luvisol
11	1.14	208	365	206	gleysol
12	1.23	182	335	209	gleyic luvisol
14	1.19	263	385	185	gleyic luvisol
15	3.39	259	378	186	gleyic luvisol
17	1.04	242	372	196	gleyic luvisol
19	4.14	286	390	187	gleyic luvisol
20	2.22	228	427	212	gleyic luvisol
21	1.76	214	375	204	gleyic luvisol
23	1.43	242	392	196	gleyic luvisol
24	4.29	244	410	grassland	gleysol
25	0.71	226	425	forest	gleysol
26	1.53	227	351	forest	gleysol
27	0.89	219	355	205	gleysol
28	0.74	238	412	205	gleysol
Average	1.95	228	365	202	

4. Discussion

Estimations of NO_3^- reduction in the unsaturated zone and the groundwater body often do not consider the deep vadose zone below the root zone or estimate them to be negligible (Fraters et al., 2006; Chen et al., 2018). Often transport modelling is done in the vadose zone. Rock and Kupfersberger (2019) even combine a 1D SIMWASER/STOTRASIM model with a 2D (vadose zone) Feflow model (groundwater). In addition, calculations of NO_3^- storage and travel time in the vadose zone are equally common. Turkeltaub et al. (2020) predict regional-scale groundwater recharge and NO_3^- storage and likewise, Turkeltaub et al. (2018) calculate the travel time of NO_3^- through the vadose zone. However, modelling of denitrification is very rare. Our results indicate that this zone appears to be of underestimated importance in this regard and should therefore be included in nutrient cycle considerations. The soil types are crucial, as they can bring microbially usable organic matter with the percolating water into deeper vadose zones. Since measured laboratory data are available from the soil profiles, an estimation can be made of how realistic the presented model is and where it is possibly limited or has optimization potential.

The amount of N in the soil can change significantly due to natural processes, the most relevant of which are organotrophic and lithotrophic denitrification. The calculated input using the measured autumn N_{min} values results in an input value which is taken as an average value for all fields. The calculated amount of percolating water and the average field capacity in the root zone as well as the residual N quantity are included in the calculation. The equation according to Renger (2002) for the calculation of the quantity of percolating water for the field sites has a high multiple Pearson correlation coefficient R of 0.84 (Eqs. (2) and (3)). Eqs. (2)–(4) show that the depth infiltration increases with increasing potential precipitation but decreases with increasing plant-available soil water and potential evapotranspiration. Consequently, a decrease in depth infiltration can be expected in the future, as potential evapotranspiration will increase, which will be triggered by rising temperatures in the course of climate change (Ortmeyer et al., 2021). High positive correlation coefficients R show that the relationship between deep infiltration and the used climate and soil characteristics are relatively narrow. The standard deviation for the calculated deep infiltration values is 20–30 mm/a.

The pedological recording of the depth profiles provides only a punctual insight into the subsoil of the areas. At each drilling point, there may be strong deviations from layer thickness to the structure of the subsoil. The calculated residence time for 60% of the investigated areas is 1 to 2 years. For 2 sites it is between 3 and 3.5 years, which is due to the higher groundwater table depths of 4 and 5 m. Akbariyeh et al. (2018) similarly point out that a consideration of the groundwater level plays an important role. If the groundwater level rises, it is easier to transport a large amount of N in the form of NO_3^- into the groundwater. Similarly, a study by Juntakut et al. (2019) indicates aquifers with relatively lower NO_3^- concentrations in areas with thicker vadose zones. Nevertheless, Ascott et al. (2017) demonstrate long travel times in the vadose zone in areas with thick vadose zones and extensive historical agriculture, so its NO_3^- leaching may take a long time to occur and measures such as a change in agricultural practices may have a delayed effect. In any case, mass balances show that the excess N corresponds very well to the annual N accumulation in the soil profiles (Baram et al., 2017).

The Michaelis-Menten kinetics models the degradation of N under idealized conditions. The denitrification rate k, which describes the range from which the NO_3^- reduction is limited by the NO_3^- concentration itself, appears to play a minor role in the soil type gleyic luvisol. In the case of very high N surpluses with low degradation rates, k becomes a small factor. The calculated leaching potential was determined using calculated average values. An input of 57 kg N/(ha*a) results in a concentration of 125 mg/L NO_3^- in the percolating water (Eq. (10)). The coarse soil fraction and the humus fraction in the sediment were taken

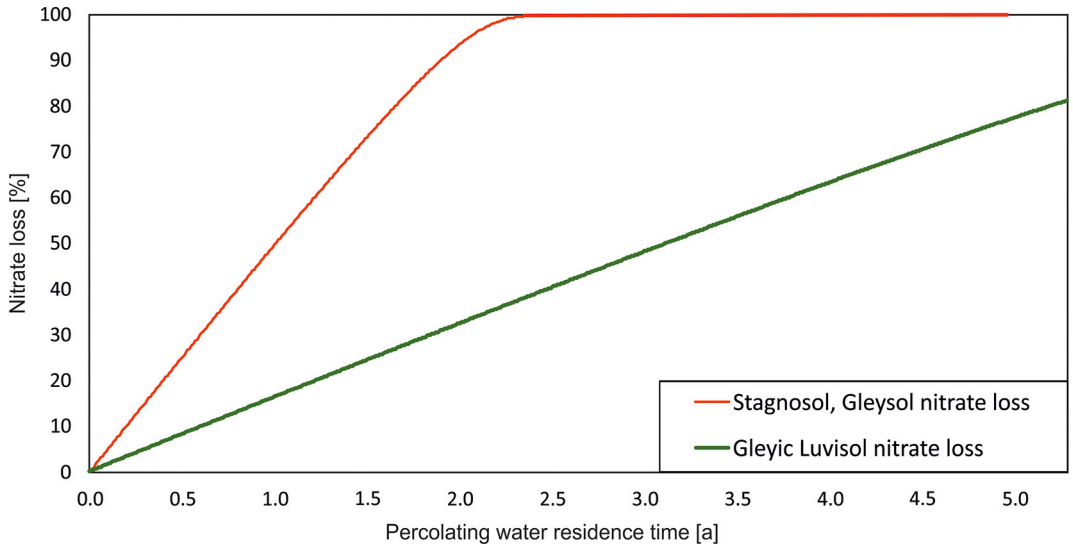


Fig. 5. Comparison of NO_3^- losses in the soil types gleysol/stagnosol and gleyic luvisol.

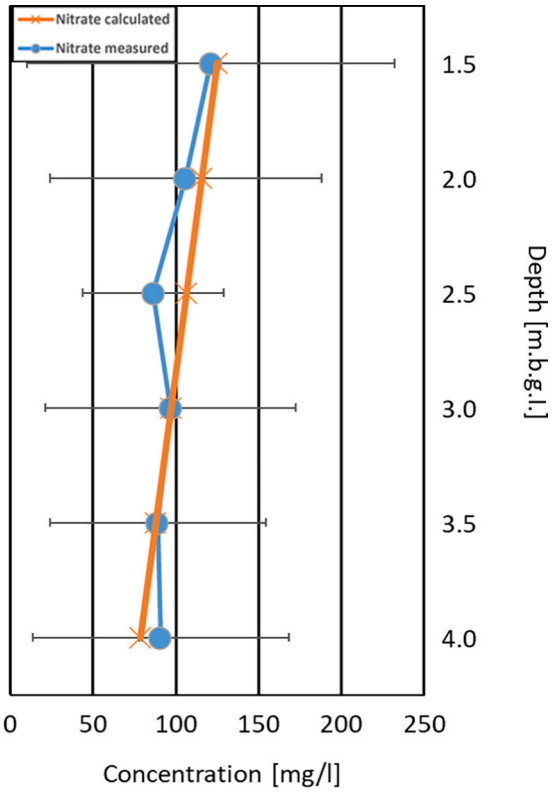


Fig. 6. Comparison of measured and calculated average NO_3^- concentrations in percolating soil water for all profiles ($n = 22$).

into account for the percolating water retention time. The sediment plays a decisive role in the residence time of the vadose zone and thus also in the time in which denitrification can take place. A coarse soil texture is prone to high NO_3^- leaching (Turkeltaub et al., 2016). Derby et al. (2009) also indicate that high NO_3^- concentrations occur in sandy soil, even when very conservative N rates are used. Intensive irrigation increases the rate of NO_3^- leaching to groundwater (Juntakut et al., 2019). A study by Akbariyeh et al. (2018), shows sediment types with higher saturated hydraulic conductivity and lower residual water content have lower water holding capacity, which increased both water infiltration rates and NO_3^- leaching rates. In the present study, measured laboratory value in the first 0.5 m below the root horizon is 121 mg/L on average for all profiles, so there is a deviation of only 3% between modelled and measured data. Sites 24, 25 and 26 were not considered because they are not cultivated arable land.

Fig. 7 shows a summarized comparison of the calculated and the measured results. The input of N as well as the calculated values of the usable field capacity, the field capacity, the amount of percolating water, the resulting NO_3^- concentration and its reduction below the root zone are altogether consistent. Calibration of the model with measured laboratory data can therefore be considered successful. The unit mg/L was chosen to understand the potential input of NO_3^- into the aquifer by the percolating water. The NO_3^- measured by the N_{min} is dissolved and carried into the deep vadose zone under the root zone. The comparison (Fig. 7) shows a good agreement of the results with the real measured values.

5. Conclusion

The NO_3^- problem in groundwater and drinking water has aggravated over the last decades (Ward et al., 2018). Due to intensive agriculture, high N doses reach the soil, which are subject to transport and transformation processes in the vadose zone. To quantify the N input into the soil zone, the autumn N_{min} is used which provided the information necessary for calculating NO_3^- shift and thus the residence time in the unsaturated zone. Denitrification potential in the unsaturated zone is determined according to the DENUZ model (Wendland, 2010). The usable field capacities and the resulting groundwater recharge were calculated. Soil types were determined and assigned a maximum denitrification rate. These data were combined with the N input and the degradation kinetics of the Michaelis-Menten equation. This resulted in the degradation potential below the root zone of the individual studied sites. Average calculated values were in good agreement with the averaged measured laboratory results.

We conclude that our initial hypothesis (substantial NO_3^- degradation in the deep vadose zone leading to unexpectedly low groundwater conditions despite massive surface N input) can be verified. The developed modelling approach is a promising tool to assess N degradation in the vadose zone, it can be applied for an improved forecast of NO_3^- levels in groundwater in affected areas using relatively easily determinable input data. It investigates a section of the N flux that is mostly neglected, focusing on the previously often underestimated denitrification potential in the deep vadose zone, between the root zone and the groundwater table. This zone should be increasingly taken into account in future

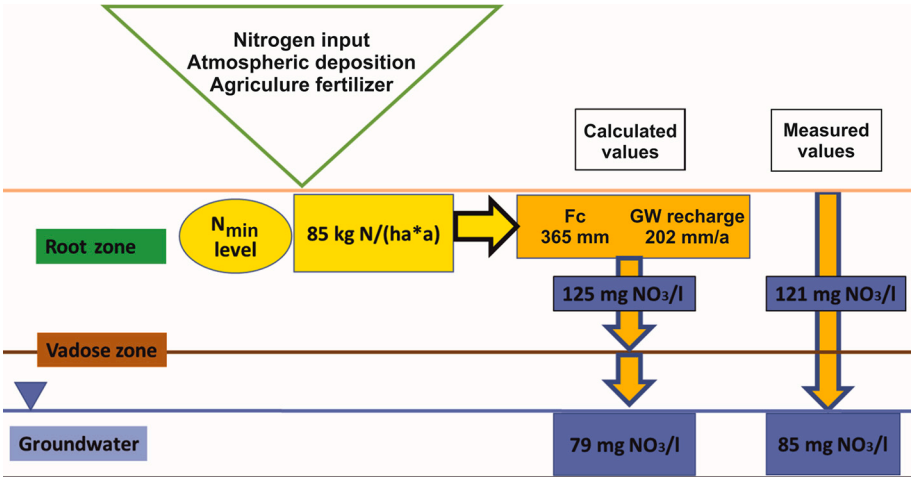


Fig. 7. Comparison of the NO_3^- balance for calculated and measured results.

studies on the nitrate problem, still one of the most pressing groundwater quality concerns on a global scale.

Declaration of Competing Interest

Authors declare that there is no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jconhyd.2021.103843.

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