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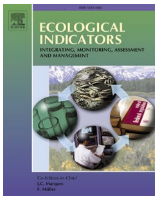

The derivation of denitrification conditions in groundwater: Combined method approach and application for Germany

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ABSTRACT

Denitrification in groundwater is an important process that helps to maintain environmental standards, yet there are very few studies that determine the spatial variation of denitrification conditions in aquifers on a regional scale. We introduce a procedure to derive spatially continuous estimates of denitrification conditions in groundwater based on the interpolation of measurements of the redox-sensitive parameters oxygen, nitrate, iron, manganese and DOC, combined with the quantification of denitrification using a 2D-hydrodynamic model based on first-order reaction kinetics. We applied this procedure to Germany, using measured values from more than 24,000 groundwater monitoring sites from 2007 to 2016. Annual concentrations of the five parameters at the monitoring sites were regionalized using an optimized, iterative inverse distance weighting procedure within 15 aquifer typologies for spatial delineation. The annual grids (2007–2016) of each parameter were then overlaid and a median over time was calculated. Discrete ranks were then assigned to the concentrations of each parameter based on their redox class, and ultimately, after overlaying the five parameters, a mean value was calculated describing the nitrate degradation conditions in groundwater. After assigning half-life times and reaction constants to those denitrification conditions, we quantified denitrification in groundwater using the hydrodynamic model WEKU.

To assess the plausibility of the derived denitrification in groundwater, we compared our results with the proportion of denitrified nitrate determined with the N_2/Ar method at 820 groundwater monitoring wells in three German Federal States, which showed an overall good agreement. Accordingly, the method presented here is suitable to be used for the regionally differentiated derivation of denitrification conditions in groundwater. For regions with denitrifying groundwater conditions, the results provide an explanation for frequently observed discrepancies between high nitrate emissions from the soil and low nitrate concentrations in the groundwater of intensively used agricultural areas.

1. Introduction

To ensure good water quality in groundwater bodies as well as their sustainable use, we must improve our understanding of threats to groundwater quality (Lapworth et al., 2022). As is the case in many countries, groundwater resources in Germany are heavily polluted by nitrate in some regions (Sundermann et al., 2020), and directives such as the EU Water Framework Directive (EU-WFD, 2000) and the EU Nitrates Directive (European Parliament and Council of the European Union, 1991) provide guidance for monitoring practices and strategies to reduce nitrate pollution. Spatially continuous estimates of nitrate concentrations in groundwater bodies are typically derived by process-based models (e.g., Kuhr et al., 2013; Merz et al., 2009; Wendland et al., 2020), and a vital input to such models is gridded information describing the denitrification potential of aquifers (Busico et al., 2020).

The amount of denitrification that occurs in an aquifer is a function

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of the hydrochemical groundwater conditions (Rivas et al., 2017) and the residence time in the aquifer (Green et al., 2016). In regions where nitrate degradation in groundwater is possible, the nitrate load of groundwater can be significantly reduced even in the case of high nitrate inputs from the soil (Eschenbach et al., 2015; Wendland et al., 2020). This also applies for groundwater-borne nitrate inputs into surface waters (Kunkel et al., 2007). Accordingly, regionally differentiated determination of nitrate degradation conditions in aquifers is an important site-parameter to quantify denitrification in groundwater and to explain any mismatches between high nitrate outputs from soil and low measured nitrate concentrations in groundwater and in surface waters.

Various studies have attempted to map the spatial variation of denitrification conditions, usually as an intermediate step to quantify nitrate concentrations in groundwater. For example: Merz et al. (2009) used the geochemical proxies redox potential and Fe-concentration to parameterize and regionalize denitrification potential over the German state of Brandenburg; and Knoll et al. (2020) used a four-point classification scheme defined by LAWA (2018) for O_2 and Fe concentrations to build a random forest model, with the use of spatial environmental predictor variables, to create a gridded dataset of redox conditions. These studies typically use a limited selection of measured hydrochemical parameters, therefore omitting potentially important information for the characterization of denitrification conditions. Also, to the best of our knowledge, there is no literature that attempts to verify the quality of spatially continuous estimates of denitrification potential in groundwater.

In this study, we introduce a combined methodology for mapping denitrification in groundwater based on a rank-based approach using-five commonly measured groundwater parameters, a deterministic interpolation method and spatial, petrographic and hydrodynamic information on aquifer typologies.. In addition, we present a method for a plausibility assessment of these estimates, based on comparisons with N_2/Ar measurements. Within the scope of the AGRUM-DE project (Schmidt et al., 2020; Wendland et al., 2022), both the characterisation and plausibility assessment are performed for the case study of Germany. Specifically, this paper addresses the following questions:

- Which hydrochemical groundwater parameters are most suitable to derive spatially continuous estimates of denitrification conditions in groundwater?
- How can this information be combined with a model based on first-order reaction kinetics to quantify denitrification rates?
- Can the plausibility of the derived denitrification kinetics be verified using N_2/Ar measurements?
- Based on the case study for Germany, can discrepancies between high nitrate outputs from the soil and low measured nitrate concentrations in groundwater and surface waters be explained?

2. Theoretical background

2.1. The process of denitrification

Denitrification is a bacterially mediated redox reaction, in which nitrate (NO_3^-) is reduced to gaseous nitrogen oxides or molecular N_2 under anaerobic conditions. The denitrifiers, which are all facultative anaerobes, adhere to the rock matrix as a biofilm.

Denitrification processes that rely on organic carbon sources as reducing agents (electron suppliers) are referred to as heterotrophic (Rivett et al., 2008). If, on the other hand, nitrate degradation takes place with the involvement of iron sulfides such as pyrite as a reducing agent, it is referred to as autotrophic denitrification (Korom, 1992). In heterotrophic denitrification, the digestibility of the organic substance in groundwater as a reducing agent plays a primary role for the denitrifiers. Low-molecular and dissolved organic carbon (DOC) compounds, such as cellulose, glucose or fulvic and humic acids, can be more easily converted by the denitrifiers than more complex, mostly fossil, solid organic compounds, such as wood, peat or lignite (Pätsch, 2006).

Organic carbon compounds in aquifers often originate from solid residues of dead organisms (flora and fauna) that were embedded in the sediments that build up the aquifer (DVGW, 2015). As the reactivity of these solid organic carbon compounds, e.g. lignite particles, is poor, their exploitability for denitrifiers is low, even when these substances are found in high concentrations (DVGW, 2015; Weymann et al., 2010). Heterotrophic denitrification in groundwater is accordingly limited by the availability of DOC (Rivett et al., 2008), i.e., it is limited to near-surface groundwater. According to Well et al. (2005), there is a low relation between DOC and denitrification in near-surface groundwater of hydromorphic soils whereas the particulate organic C content is decisive. Moreover, the contribution of DOC to denitrification in groundwater has been shown to be insignificant in incubation studies (Siemens et al., 2003). With increasing depth, heterotrophic denitrification becomes less prevalent as autotrophic denitrification plays a more decisive role

In autotrophic denitrification, metal sulfides, usually sulphur-iron compounds (pyrite), play a major role in nitrate reduction in aquifers, e.g. in northern Germany. Kölle (2017) states that in a pyrite- and carbon-containing aquifer almost all denitrification occurs with pyrite as a reactant. In contrast, the solid organic residues in aquifers are more difficult to access for denitrifiers than the reduced sulphur-iron compounds. Therefore, nitrate reacts in groundwater considerably faster with pyrite than with fossil carbon compounds (Postma et al., 1991).

Denitrification in the aquifer stops once the reactive substances (pyrite, DOC, solid organic carbon) involved in nitrate degradation have been consumed. Rohmann and Sontheimer (1985) refer to this process as “nitrate breakthrough”.

2.2. Redox-sensitive parameters in groundwater

Hydrochemical analyses of groundwater provide valuable information regarding denitrification conditions in an aquifer, through concentration data for the redox-sensitive parameters described below.

2.2.1. Oxygen

If the oxygen in the unsaturated zone is not completely depleted for oxidation processes, it reaches the groundwater with the leachate. In general, the measured concentrations of dissolved oxygen in groundwater lie between less than two and approximately 10 mg O_2/L. According to Kölle (2017) an oxygen concentration of approximately 10 mg O_2/L in groundwater indicates an oxygen saturation at groundwater recharge temperatures of 8 to 10 °C which is typical for Germany. In the aquifer, the oxygen input with the leachate is consumed for the oxidation of various inorganic and organic substances. For the microorganisms in groundwater, oxygen respiration means the highest energy gain, which is why they only switch to nitrate respiration at very low concentrations of dissolved oxygen.

Studies that address nitrate degradation in groundwater unanimously report that low oxygen concentrations are a basic prerequisite for denitrification (Stuart, 2018). In most cases, oxygen concentrations in the range of less than 1 and up to 2 mg O_2/L are regarded as the boundary between nitrate-degrading and non-nitrate-degrading conditions in groundwater (DVWK, 1988; Ebeling et al., 1988; Obermann, 1981; Rissmann, 2011). However, even at oxygen concentrations of about 5 mg O_2/L, denitrification processes have been detected (Hölting, 1996; Rohmann & Sontheimer, 1985). In this context, Pätsch (2006) found that even in aquifers with oxidizing conditions, denitrification can occur locally due to local oxygen depletion of microorganisms in the biofilm.

2.2.2. Nitrate

Naturally occurring nitrate in groundwater from inorganic nitrate sources does not exist. The reason for this is that all nitrate salts are very easily soluble in water, so that during the geologic eras in humid climate zones no nitrate rocks were formed from which nitrate can be dissolved by circulating groundwater (Kölle, 2017). Nitrogen released from bedrocks contributes to the natural nitrate concentration in groundwater (Panno et al., 2006), though the resulting nitrate concentrations in (oxidized) groundwater are negligible. Other naturally occurring sources of nitrate in groundwater include organic substances. While the amount of (fossil) organic substances in groundwater is in general quite low, the amount of organic and inorganic nitrogen-containing compounds occurring in soil represents a significant nitrogen source. In the soil nitrogen cycle, these compounds are transferred into each other by microorganisms through metabolic processes. Consequently, in natural ecosystems only small amounts of nitrate are leached from the root zone and enter the aquifer. The nitrate concentration in groundwater from all these natural sources rarely exceeds 10 mg NO_3^-/L (Rahman et al., 2021; Wendland et al., 2005).

Therefore, large-scale nitrate concentrations in (oxidized) groundwater above 10 mg NO_3^-/L can be interpreted as a definite indication of large-scale anthropogenic pollution by agriculture and settlements, including atmospheric deposition (Dubrovsky et al., 2010; Wendland & Kunkel, 1999). However, the reverse conclusion that an aquifer with nitrate concentrations below 10 mg NO_3^-/L is equivalent to an anthropogenically unaffected aquifer cannot be made for reduced aquifers because denitrification processes may be occurring.

2.2.3. Iron

Iron is the fourth most abundant element in the earth's crust and a component of almost all soils and rocks; it is therefore detectable in most groundwater bodies. Source rocks include siliceous iron minerals, such as olivine, as well as minerals formed during weathering processes such as iron sulfides (e.g. pyrite), iron oxides (e.g. hematite) and iron hydroxides. In oxidized groundwater, iron is detectable only in traces, because in this environment it is present only as oxidized trivalent iron hydroxide (Fe^{3+}), which shows a poor solubility at typical groundwater pH-values. For this reason, there is no significant input of iron into groundwater with the leachate; only in strongly acidic waters ($pH < 2.5$), dissolved trivalent iron is an issue (Kölle, 2017).

In contrast to trivalent iron, bivalent iron (Fe^{2+}) is relatively water-soluble in groundwater from pH 5 to pH 9, meaning that all almost all iron dissolved in groundwater is present as bivalent iron. High bivalent iron concentrations in groundwater are usually of natural origin and representative for oxygen-poor ("reduced") groundwater (Palmucci et al., 2016; Postawa et al., 2013). Matthess (1990) indicates a typical Fe^{2+}-concentration range of reduced groundwater between 1 and 10 mg Fe^{2+}/L. As a rule, a bivalent iron concentration > 0.2 mg Fe^{2+}/L is a reliable orientation value for indicating the transition range from an oxidizing to a reducing environment, and thus nitrate-degrading, environment in the aquifer (DVWK, 1992; Wendland & Kunkel, 1999). Consolidated pyrite-bearing rocks are an exception to this rule. Groundwater circulating in these rocks often exhibits elevated iron concentrations, although the denitrification capacity of groundwater is limited (Wendland et al., 2007).

2.2.4. Manganese

Manganese displays similar geochemical properties to iron and is therefore usually found in association with iron (Kölle, 2017). Due to its low occurrence in rocks, manganese concentrations in groundwater are usually below 1 mg/L and thus significantly below iron concentrations (Koopmann et al., 2020; Kunkel et al., 2004). Manganese accumulates very strongly in plants, so that its occurrence in groundwater can be traced back to fossil plant material, that has reached the groundwater from the earth's surface.

As with iron, manganese inputs into groundwater via leachate are negligible (Wendland et al., 2005). In an oxidized environment, manganese is mainly present as precipitated trivalent manganese oxide (Mn^{3+}) or tetravalent manganese oxide (Mn^{4+}). After nitrate reduction, both species can serve as oxidants for denitrification processes in groundwater, being reduced to dissolved divalent manganese (Mn^{2+}). In oxidized groundwater, the concentration of bivalent manganese is typically below 0.05 mg Mn^{2+}/L, whereas in reduced groundwater it often exhibits valuesbetween approximately 0.1 and 0.5 mg Mn^{2+}/L (Jaudon et al., 1989).

2.2.5. Dissolved organic carbon (DOC)

Due to the fact that the particulate organic C content (C_{org}) of an aquifer, which can be regarded as a decisive parameter for indicating denitrification processes in groundwater (Well, 2005), is often not measured in groundwater sampling, theDOC has been included.DOC is a sum parameter for the organic carbon compounds dissolved in groundwater (primarily humic and fulvic acids). Depending on the site conditions, DOC concentrations in groundwater cover a wide range of values. Most DOC in the aquifer is infiltrated via groundwater recharge and originates from decomposing organic materials. Groundwater from glacial sand and gravel deposits overlaid by organic rich sediments may contain DOC concentrations higher than 15 mg DOC/L (Artinger et al., 2000) and often correlates with anaerobic groundwater conditions (Kunkel et al., 2004). According to Regan et al. (2017), Concentrations in groundwater above 4 mg DOC/L may also indicate anthropogenic contamination issues such as the application of manure.

The DOC concentration originating from solid-bound C_{org} compounds is generally very low. In unconsolidated sand and gravel deposits, the release of DOC from solid-bound C_{org} compounds (e.g. coal particles, wood) is possible. Their reactivity decreases with the age of the sediments (Appelo & Postma, 2005). In some groundwater bearing rocks (e.g. crystalline rocks), solid-bound C_{org} compounds may not occur at all. Consequently, the DOC concentrations in groundwater from bedrocks rarely exceeds 0.75 mg/L and often correlates with aerobic (oxidized) groundwater conditions (Kunkel et al., 2004).

Although Cremer et al. (2018) conclude that DOC plays a minor role in denitrification, as 1 DOC mg/L can only reduce 4 mg NO_3^-/L, the probability of denitrification in groundwater increases with increasing DOC concentration. DOC concentration is thus another indicator of reduced conditions in groundwater.

2.2.6. pH

Whereas the optimal pH range for heterotrophic denitrification is in a slightly alkaline environment between pH 7 and pH 8 (Knowles, 1982; Rheinheimer et al., 1988), the organisms responsible for autotrophic denitrification are active over a wide pH range (Mehranfar & Well, 2002). At a pH of 3.5, this effect is already measurable (Pätsch et al., 2003). According to Kludt (2021), heterotrophic denitrification is favored by pH values of approximately 6 – 10 and autotrophic denitrification by pH values between 2 and 9.5.

2.2.7. Redox potential

Redox potential describes the concentration ratio of oxidized and reduced substances and thus the electrochemical conditions in water (Baier, 2015), with nitrate typically found in groundwater with redox potential values higher than approximately 200 mV (Krajnov & Voigt, 1990). However, during groundwater sampling the measured value may be influenced by external factors, such as contact with atmospheric oxygen (Baier, 2015). For this reason, Krause calculated the redox potential indirectly via the Nernst equation from the parameters bivalent iron and pH (Krause, 1990). This revealed a general discrepancy between the expected and the calculated redox potential, which could be because the sampled groundwater represents a mixture of groundwaters with different redox values at some groundwater monitoring wells. According to Kofod (2000), the discrepancy may also be due to the interaction of the different redox couples and the corresponding microorganisms involved in the redox reactions. Since all microorganisms have their optimal living conditions at varying pH ranges (Merkel et al., 1993), the redox potential depends on more than just the Fe-pH interplay. Therefore, the reliability of measured (or calculated) redox potentials is limited. Lastly, the redox potential is often not determined during groundwater sampling.

2.3. Relationship between depth and denitrification potential

The solution content of surface-near groundwater is related to the solution content of the leachate and exhibitss large variations between individual observations. In many cases the oxygen content of surface-near groundwater is high, while the reserve of pyrite or reactive C_{org} is depleted, thus impeding denitrification.

With increasing depth, aquifers generally show increasingly anoxic conditions. One reason for this is the longer reaction time of the groundwater with the rock matrix. In addition, at greater aquifer depths, the reserves of pyrite or reactive C_{org} has not yet been used up. However, it should be noted, that the (atmospheric) oxygen content in groundwater can be maintained at greater depths as long as the aquifer is free from redox reactive substances such as pyrite or reactive organic substances. The latter aquifers do not exhibit denitrifying properties.

In aquifers containing reducing substances, whether or not a sample displays denitrifying groundwater conditions is therefore often a question of the sampling depth. As described by various authors (Andersen & Kristiansen, 1984; Böttcher et al., 1989; Kölle, 1990; Kolbe et al., 2019; Korom, 1992; Tomer & Burkart, 2003), nitrate degradation can be expected in reduced aquifers, though the depth at which this occurs is site dependent (typically 1–10 m below the groundwater surface). Consequently, the surface-near groundwater of a monitoring well of a nitrate-degrading aquifer may exhibit the hydrochemical characteristics of the leachate, i.e., high oxygen and nitrate levels indicating no denitrifying properties, while deeper groundwater of a deeper monitoring well at the same location may exhibit nitrate-degrading groundwater conditions. For this reason, sampling depth is an important secondary parameter, especially for regions where aquifers exhibit denitrifying groundwater conditions. Unfortunately, a depth-graded groundwater monitoring network, from which the transition from aerobic to anaerobic groundwater can be recognized, is often missing.

3. Methods

3.1. Derivation of denitrification conditions

The denitrification conditions are derived as spatially continuous estimates following a two-step process: i) generation of spatially continuous estimates of concentrations of redox-sensitive parameters (Fe^{2+}, Mn^{2+}, O_2, NO_3^-, DOC) ii) ranking of redox potential according to indication classes of the redox-sensitive parameters and overlaying to derive a final map of denitrification conditions. These steps are described in detail in the following sub-sections. Note that the parameters defined to allocate the redox indication classes are based on available literature for Germany, and we advise that these be assessed prior to application in countries with substantially different hydrogeochemical settings.

3.1.1. Geoprocessing of redox-sensitive parameter concentrations

Based on the information in chapters 2.2.1 to 2.2.5 we identified five redox-sensitive parameters as the most suitable for deriving denitrification conditions: Fe^{2+}, Mn^{2+}, O_2, NO_3^- and DOC.

To derive the denitrification conditions in aquifers for large areas, e.g. on a nation-wide scale, the concentrations of the selected parameters were first regionalized together with information of aquifer typology to generate spatially continuous fields of estimates. This is performed with the following steps:

(1) The exclusion of monitoring sites from deep aquifers with filter depths of $>$ 50 m below ground level for unconsolidated rocks and $>$ 95 m below ground level for consolidated rocks.
(2) For groundwater monitoring sites where multiple samples are available within one year, calculation of an arithmetic mean of analyzed redox parameters per year. This ensures that each measuring point is equally weighted in the further evaluation (see point 4).
(3) Delineation of areas that exhibit different aquifer typologies. An aquifer typology spatially groups aquifers with comparable petrographic and hydrodynamic conditions, organizing the complexity of groundwater resources into a simplifying system (Wendland et al., 2008). Those aquifers will likely exhibit similar solution contents (Wendland et al., 2005).
(4) Spatial interpolation of the concentration measurements using the Inverse Distance Weighting (IDW) method (Shepard, 1968) for each aquifer typology for each redox parameter and each year. The determination of the optimal IDW parameters 'search neighborhood' and 'power' is computed iteratively for each interpolation. For each predefined pair of IDW parameter values, a leave-one-out cross-validation (LOOCV) (Sammut & Webb, 2011) is used to determine RMSE (root-mean-square error) that indicates the deviation of observed and simulated concentrations resulting from the interpolation. The pair of values with the lowest RMSE is selected as the best option for interpolation.
(5) The five interpolated separately for the individual aquifer typologies for each year of the evaluation period are spatially combined. In this way, one data set (map) with concentration values covering the entire study area is generated for each redox parameter for each year.
(6) The annual data sets (maps) of concentrations of the five redox parameters are merged individually using the median, resulting in multi-year averaged data sets (maps) of concentrations for the five redox parameters.

3.1.2. Ranking of concentration classes

To categorize groundwater according to the solution content of the five selected redox-sensitive parameters into nitrate-degrading (reduced), non-nitrate-degrading (oxidized) and intermediate concentration classes, reference values of the concentrations have been identified that characterize the transition from a reduced environment to an oxidized environment (Ackermann et al., 2015; Hannappel, 1996; Heidecke et al., 2015; Hölting, 1996; Kuhr et al., 2013; Kunkel et al., 1999; Kunkel et al., 2004; Leuchs, 1988; Obermann, 1981; Palmucci et al., 2016; Wendland, 1992; Wendland et al., 2015).

After a long residence time in the aquifer, groundwater from nitrate-degrading aquifers typically exhibits oxygen concentrations of $<$ 2 mg O_2/L (Palmucci et al., 2016). The substantial absence of oxygen and nitrate is usually associated with bivalent iron concentrations of $>$ 0.2 mg Fe^{2+}/L, divalent manganese concentrations of $>$ 0.05 mg Mn^{2+}/L and DOC concentrations of $>$ 0.75 mg DOC/L (Kunkel et al., 1999). High DOC contents can occur regionally in reduced aquifers in combination with high bivalent iron and manganese contents, but there are also aquifers in which either exclusively elevated bivalent iron / bivalent manganese contents or exclusively elevated DOC contents occur.

Furthermore, in many cases not all measured concentrations of the five selected parameters indicate uniformly reduced or oxidized groundwater conditions at a monitoring site. For example, a groundwater sample may indicate oxidized groundwater conditions based on the observed concentrations of nitrate and oxygen, while indicating reduced groundwater conditions for the observed bivalent iron concentration. According to Kölle (2017) such groundwater compositions can occur when sampling of a mixture of different groundwaters, e.g., from different depths, has occurred. It is also possible that such a groundwater composition results from iron-rich groundwater-bearing rocks, where the observed bivalent iron concentration reflects the dissolution equilibrium of the iron- containing minerals in groundwater rather than indicating of reduced aquifer conditions. Similarly, regionalized medium to high nitrate concentrations in groundwater (e.g. above

10 mg NO_3^-/L) are not necessarily an indicator of oxidized groundwater conditions, since a large portion of the nitrate input into the aquifer may have already been denitrified (Kölle, 2017). We therefore recommend to simultaneously use the observed concentrations of all five selected parameters to ensure the optimal classification of the redox status and denitrification conditions in groundwater. For simplification, the time-dependent aspect of depleting reactive substances ("nitrate breakthrough") has not been considered.

Due to the different concentration ranges in which the redox-sensitive parameters occur in groundwater (Kunkel et al., 1999; Kunkel et al., 2004), the concentration ranges should first be normalized by assigning ranks (see Table 1). This procedure allows an equal weighting for all five parameters in terms of identifying denitrification conditions. The highest class (Rank 3) contains concentrations in ranges that are typical for reducing and thus nitrate-degrading aquifers. Rank 2 and Rank 1 cover the transitional range of concentrations that do not allow a clear assignment to oxidizing or reducing hydrochemical conditions. In the lowest class (Rank 0), the concentrations lie in a range that is typical for oxidizing and thus non-denitrifying aquifers (Table 1).

1. The multi-year averaged datasets of concentrations for each redox parameter (see Chapter 3.1.1) are classified into discrete redox indication classes (ranks) ranging from 0 (low nitrate degradation capacity) to 3 (high nitrate degradation capacity) using the ranges listed in Table 1.
2. The five resulting datasets (maps) of the redox indication classes between 0 and 3 are overlaid. An arithmetic mean is calculated, which indicates the denitrification conditions in groundwater. Unlike the discrete ranks in the values of the individual redox parameters, the final map can show decimal values between 0 and 3.

3.2. *Quantification of denitrification using kinetics*

The denitrification conditions in groundwater impact the denitrification kinetics in groundwater and consequently the denitrification rates in groundwater. More specifically, denitrification rates in groundwater from denitrifying aquifers should be higher than denitrification rates in groundwater from non-denitrifying aquifers.

We implemented the WEKU model, which is a two-dimensional model that calculates residence times and denitrification rates in groundwater based on a first-order reaction kinetics (Böttcher et al., 1989; Kunkel & Wendland, 1997; Kunkel et al., 2007; Wendland et al., 2021). Extensive studies on nitrate degradation in groundwater in Thülsfelde (Pätsch, 2006) and in the Fuhrberger Feld near Hanover indicated denitrification kinetics in groundwater between 0.34 and 0.56 a^{-1} for the local reduced groundwater conditions (Böttcher et al., 1989), which corresponds to a half-life time of denitrification of 1.2 to 2.1 years. Pätsch et al. (2003) determined comparable half-life times of 1.2 to 3.4 years in other study areas in Lower Saxony with reduced groundwater conditions. Other data from the literatur (Ackermann et al., 2015; Heidecke et al., 2015; Kuhr et al., 2013; Kunkel et al., 1999; Kunkel et al., 2004; Merz et al., 2009; Uhlig et al., 2010; van Beek, 1987; Wendland, 1992; Wendland et al., 2015), were used to define ranges of half-lives and reaction constants. These information were plotted against the denitrification conditions (0 to 3). An approximate exponential relationship between half-life times and denitrification conditions can be observed whereas half-life times are exponentially declining (and reaction constants exponentially increasing) with increasing denitrification potential. Considering the ranges in Table 2, the curve is slightly adjusted in a way that harmonizes the results of the WEKU model with the results of the N_2/Ar measurements described in Chapter 5.3.

Table 1
Redox indication classes of the five redox parameters.

Parameter	Ranks for allocated redox indication classes			
	0 (oxidized)	**1** (transitional ox.) range transitional range	**2** (transitional red.) range	**3** (reduced)
O_2	> 6 mg/L	> 4 – 6 mg/L	> 2 – 4 mg/L	< 2 mg/L
NO_3^-	> 10 mg/L	> 5 – 10 mg/L	> 1 – 5 mg/L	< 1 mg/L
Fe^{2+}	< 0.1 mg/L	> 0.1 – 0.3 mg/L	> 0.3 – 1 mg/L	> 1 mg/L
Mn^{2+}	< 0.05 mg/L	> 0.05 – 0.1 mg/L	> 0.1 – 0.2 mg/L	> 0.2 mg/L
DOC	< 0.75 mg/L	> 0.75 – 1.5 mg/L	> 1.5 – 3 mg/L	> 3 mg/L

3.3. *Plausibility assessment of derived denitrification in groundwater*

3.3.1. *N_2/Ar method*

To verify the relationship between the derived denitrification conditions and the assumed kinetics of denitrification in groundwater, N_2/Ar measurements were used to determine the extent of nitrate degradation in groundwater by the measurement of N_2 excess in groundwater (Böhlke, 2002; Vogel et al., 1981). N_2 excess is calculated from the measured concentrations of molecular nitrogen (N_2) and argon (Ar) in groundwater samples (Weymann et al., 2008). In contrast to molecular nitrogen, argon as a noble gas does not react as part of biochemical conversion processes like denitrification in groundwater. Groundwater recharge temperatures of about 10 °C, which is typical for Germany, and a composition of the air in the unsaturated zone similar to that of the atmosphere results in concentrations of dissolved molecular nitrogen of 17.7 mg/L and of argon of 0.67 mg/L in newly recharged groundwater originating from the air. Denitrification in the aquifer increases the concentration of molecular nitrogen, thus shifting the N_2/Ar ratio to higher values. The N surplus calculated in this way can then be attributed to denitrified nitrate in the groundwater.

N_2/Ar measurements can be used to determine both the initial nitrate content in a groundwater sample at the time that groundwater recharge occurred as well as the nitrate removal by denitrification on the flow path from the groundwater surface to the monitoring well. Excess air (N_2 and Ar concentrations above the expected concentrations resulting from dissolution of air in groundwater) from dissolving entrapped air at the groundwater surface as well as in situ degassing (e.g., resulting from oversaturation of groundwater with molecular nitrogen due to intense denitrification) is determined based on the deviation of Ar concentration from the expected concentration (Weymann et al., 2008).

In summary, the N_2/Ar-measurements in groundwater allow conclusions to be drawn about the extent of denitrification in groundwater, since the nitrogen gas formed during denitrification in the unsaturated zone has already volatilized. For this reason, the N_2/Ar method reflects denitrification in groundwater only (Schreiber et al., 2020). Furthermore, the N_2/Ar method calculates an initial nitrate concentration in the groundwater for the time of the transition of the leachate into the saturated zone and time-delayed by the travel time of groundwater from

Table 2
Assignment of point values of denitrification conditions to documented ranges of half-life times and rate constants of denitrification in groundwater.

Point values of denitrification conditions	Range of half-life times of nitrate in groundwater [a]	Range of reaction constants (KN) of denitrification in groundwater [a^{-1}]
Denitrification probable (value of 2–3)	0.5 – 2	0.3 – 1.4
Denitrification intermediate (value of 1–2)	2 – 8	0.1 – 0.3
Denitrification insignificant (value of 0–1)	8 – 30	0.02 – 0.1

this point to the groundwater measuring point (Eschenbach et al., 2018). Therefore, N_2/Ar measurements are very suitable to assess the plausibility of the derived denitrification conditions in groundwater and in combination with groundwater travel times the assumed kinetics of denitrification in groundwater allow the plausibility check of the modeled denitrificationby comparison with measured values of the completed denitrification along the groundwater flow paths.

3.3.2. Denitrification over inflow areas of groundwater monitoring wells

The assumed denitrification kinetics are used to calculate denitrification rates in groundwater. First, the groundwater inflow areas of the N_2/Ar monitoring wells were derived (Wolters et al., 2021). Subsequently, the WEKU-model was applied to quantify denitrification rates for the groundwater inflow areas of the N_2/Ar monitoring wells, based on Equation (1):

$$N(t) = N_0 \times exp^{-KN \times t} \tag{1}$$

In the WEKU model, nitrogen output from groundwater (N(t)) is determined as a function of reaction constants (representing half-life times, see Table 2) of denitrification in groundwater (KN), nitrogen input into recharged groundwater (N_0) and groundwater travel time (t). Travel time is calculated by adding the individual flow times in the grid cells along the flow path from the point of entry to the point of discharge, i.e. the N_2/Ar monitoring wells (Equation (2)):

$$t = \sum_i \frac{l_i}{v_{a,i}} \tag{2}$$

where $v_{a,I}$ is defined as the groundwater distance velocity and l_i as the flow length in the raster cell i. For calculating denitrification rates in groundwater, the reaction constants (half-life times) of denitrification in groundwater (KN) for the inflow areas of the N_2/Ar monitoring wells were taken from the derived dataset of half-life times of nitrate degradation in groundwater.

Fig. 1 llustrates the procedure for determining the degraded quantity of nitrate in the inflow area of the monitoring sites for which N_2/Ar measurements were available. Modeling denitrified nitrate at a monitoring well requires consideration of the entire flow path of groundwater in the inflow area of the well (Fig. 1, top right). Since the model is grid based, the quantity of nitrate degraded in the groundwater at a monitoring well is determined from the N input attributed to the upstream grid cells in the inflow area of the monitoring well, as well as by the groundwater velocity and the denitrification constants in those corresponding grid cells (Fig. 1, middle panels). In this case, the denitrified quantity of nitrate in the inflow area of a measuring point corresponds to the mean value of the denitrified N quantity in the grids along the flow path (Fig. 1, bottom). The corresponding mean percentage denitrified nitrate in the inflow area is then compared with the percentage denitrified nitrate calculated from the N_2/Ar measurements. This procedure

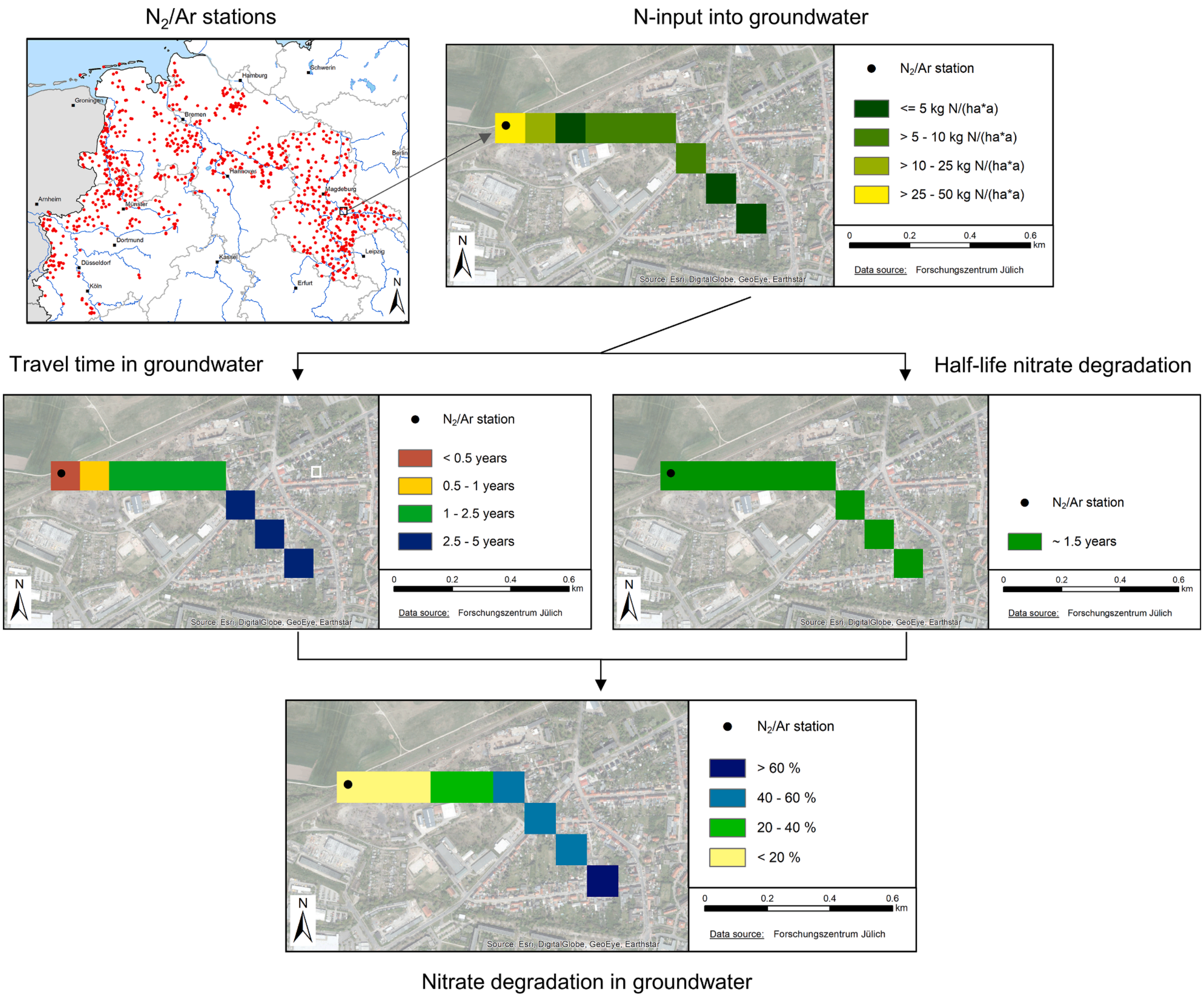

Fig. 1. Schematic representation of the procedure to determine the nitrate denitrified in the inflow areas of groundwater monitoring wells with N_2/Ar measurements.

is applied to all available groundwater monitoring stations (Fig. 1, top left).

4. Database for the case study of Germany

For the classification of the denitrification conditions in groundwater throughout Germany, we used datasets from the period 2007–2016 provided by the Federal German States via the LAWA (German Working Group on water issues of the Federal States and the Federal Government represented by the Federal Environment Ministry).

After quality control and removal of monitoring sites from aquifers that were too deep according the exclusion criteria approximately 14,800 to 21,200 monitoring stations remained for further evaluation, depending on the respective redox parameter (see Table 3). This equates to a monitoring network density of approximately 4 to 7 monitoring sites per 100 km^2 averaged over Germany which corresponds approximately to the density of monitoring network required in a general German administrative ordinance on the designation of nitrate-polluted areas (AVV, 2020). For these monitoring stations, approximately 102,000 to 161,000 measurements were available for 2007–2016 depending on the respective redox parameter, meaning that each redox parameter was recorded 6–8 times on average per monitoring station over that period.

Fig. 2 shows the locations of the groundwater monitoring sites. In regions where significant aquifers occur (e.g. Lower Rhine Bight), the station density is higher than in regions without significant aquifers (e.g. Rhenish Slate Mountains). In addition, the density of measuring stations depends on the number of installed measuring stations in the individual federal states as well as on the number of provided datasets.

The datasets of the southern federal German states, for example, comprised a much larger number of monitoring sites than the federal states to the north. hence the uncertainty of derived denitrification conditions over these southern states is lower than for the northern states. Also shown on Fig. 2 are the 15 aquifer typologies used as separate spatial reference units for the regionalization of the concentrations of the five redox-sensitive parameters. Approximately 50 % of the Germany consist of pore aquifers comprising of unconsolidated rocks, i.e. sand and gravel deposits. According to their genesis, the sand and gravel deposits can be differentiated into glacial sediments, (north) and fluviatile deposits (south and west). In central and southern Germany, the aquifers consist predominantly of consolidated rocks, such as sandstones, limestones, shales, magmatic rocks etc.

For the plausibility assessment, modeled data on average long-term nitrate input into the groundwater (N_0) and groundwater velocity (v_a) were available at a spatial resolution of 100 × 100 m (Schmidt et al., 2020; Wendland et al., 2022; Fig. 3) and were matched to the corresponding inflow areas of the N_2/Ar monitoring wells.

1,617 N_2/Ar measurements were available for 1,259 monitoring sites in the Federal German states of North Rhine-Westphalia, Lower Saxony and Saxony-Anhalt from the period 2005 – 2021. N_2/Ar measurements from these three states are assumed to be particularly well suited for this purpose because the full range of derived denitrification conditions in groundwater in Germany (Fig. 6) occur there. Hence, a high representability can be expected.

Prior to evaluation, 159 N_2/Ar monitoring sites with no or low initial nitrate content < 4 mg/L) were removed from further evaluation, as it is not possible to assess denitrification rates for such samples with the N_2/Ar method. Furthermore, we excluded 280 N_2/Ar monitoring sites for which no groundwater inflow area could be assessed. For the remaining 820 N_2/Ar monitoring sites (shown on Fig. 1, top left) mean values were calculated if monitoring sites sampled twice for different years and for multilevel monitoring wells with multiple N_2/Ar measurements at varying depths at one location.

Table 3
Evaluated groundwater monitoring stations and number of measurements for 2007–2016.

Parameter	Monitoring sites	Measurements
O_2	21,224	142,814
NO_3^-	20,501	161,210
Fe^{2+}	16,761	107,407
Mn^{2+}	16,555	105,107
DOC	14,778	101,899

5. Results

5.1. Denitrification conditions of groundwater in Germany

The denitrification conditions in groundwater throughout Germany were derived according to the geostatistical analysis described in Chapter 3 and based on the groundwater quality data described in Chapter 4. The observed concentrations of bivalent iron, bivalent manganese, nitrate, oxygen and DOC were first interpolated for the 15 aquifer typologies (Fig. 2) individually for each year of the period 2007 – 2016. This regionalization was carried out for a raster geometry with a spatial resolution of 100x100m. Subsequently, the regionalized concentrations for the 15 aquifer typologies were merged to German-wide maps.

The interpolation shown in Fig. 4 is an example for the redox parameter bivalent iron for the year 2007, a process that is repeated for each year of the period 2007–2016. As a result, 150 concentration grids differentiated according to the aquifer typology (Fig. 2) were obtained for the parameter iron (15 aquifer typologies × 10 years). From these 150 grids, 10 Germany-wide annual concentration grids were derived for the parameter iron. The same procedure was applied for the remaining four redox parameters (bivalent manganese, nitrate, oxygen and DOC).

The interpolated concentration distributions of the years 2007–2016 were then used to derive a median concentration map for each of the five redox parameters. The derived median concentrations were subsequently ranked according to the redox indication classes specified in Table 1. The general procedure of median averaging and ranking according to redox indication classes is illustrated for bivalent iron in Fig. 5.

For the final determination of the denitrification conditions in groundwater, the redox indication classes of all five redox-sensitive parameters were overlaid and averaged. The resulting values correspond to the denitrification conditions in groundwater throughout Germany (Fig. 6).

For the five maps of redox-sensitive parameters (Fig. 6, left), the highest redox indication class (3) occurs in the North German lowlands for the redox parameters bivalent iron, bivalent manganese, oxygen and DOC, indicating groundwater conditions typical for reduced groundwater conditions and thus indicating nitrate-degrading aquifers. The intermediate redox indication class (1–2) appears for the parameters bivalent iron and bivalent manganese in the surroundings of the low mountain areas in central and southern Germany and for the parameter DOC within these low mountain areas. The lowest redox indication class (0) indicates oxidized groundwater conditions and thus non-nitrate-degrading aquifers. This class occurs predominantly in consolidated rock areas, namely for the parameters bivalent iron, bivalent manganese and oxygen and for the parameter nitrate in many parts of Germany.

High values (2–3) are present in the parts of the North German Lowlands, where the redox indication classes of all redox-parameters show reduced groundwater conditions.Intermediate values (1–2) are widespread in the transitional zone between the North German Lowlands to the midland areas and additionally in same parts of the Upper Rhine Valley and the Lower Rhine Embayment. Low values (0–1) dominate in almost all consolidated rock areas and occur when none or just one redox parameter indicates reduced groundwater conditions, while all other parameters indicate oxidized groundwater conditions.

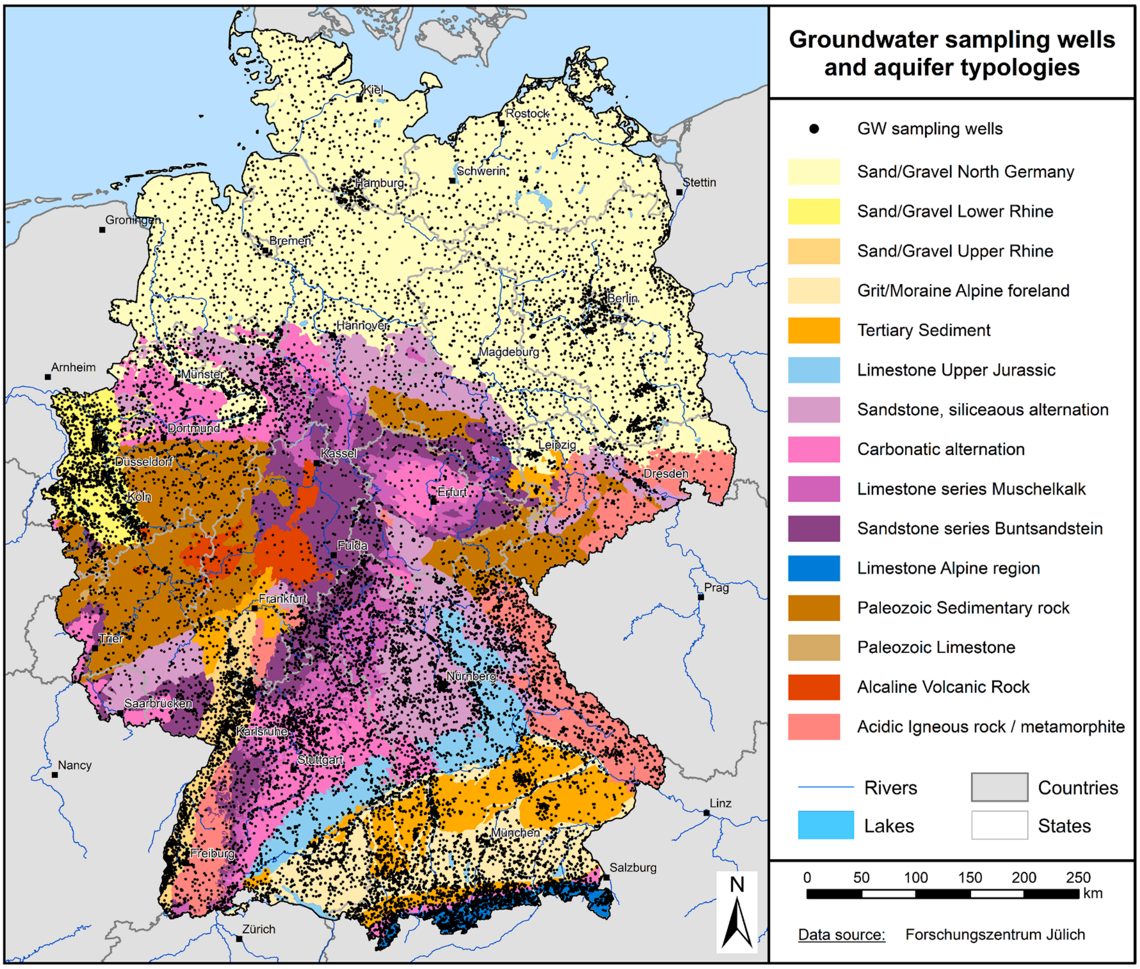

Fig. 2. Geographical locations of groundwater monitoring sites for the designation of denitrification conditions in groundwater and German aquifer typologies.

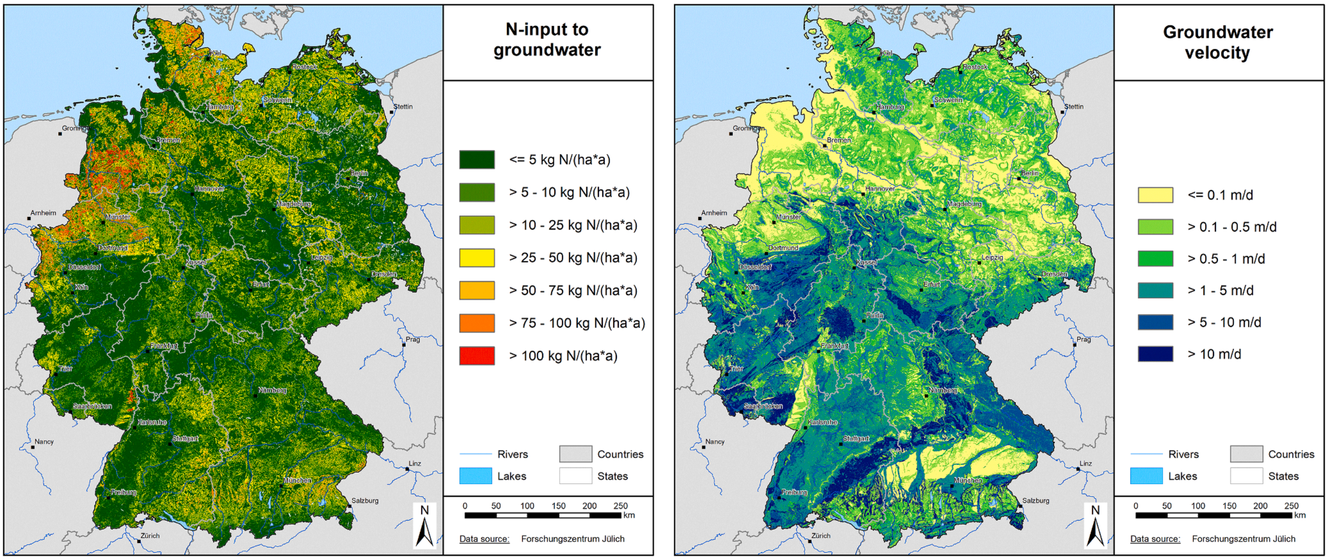

Fig. 3. *N*-input into groundwater (left) and groundwater velocity (right) determined in the AGRUM-DE-project (Schmidt et al., 2020; Wendland et al., 2022).

5.2. *Denitrification rates in groundwater*

Fig. 7 shows the regionalized half-life time nitrate degradation in groundwater resulting from linking the documented reaction constants (Table 2) with the redox indication classes 0 to 3 (Table 1 and Fig. 6, right), which indicate the denitrification conditions in groundwater.

For most aquifers in consolidated regions in Germany, Fig. 6 shows point values between 0 and 1 and thus insignificant denitrification conditions in groundwater. For such aquifers, only very few reaction constants for denitrification are documented, Merz et al. (2009) provide

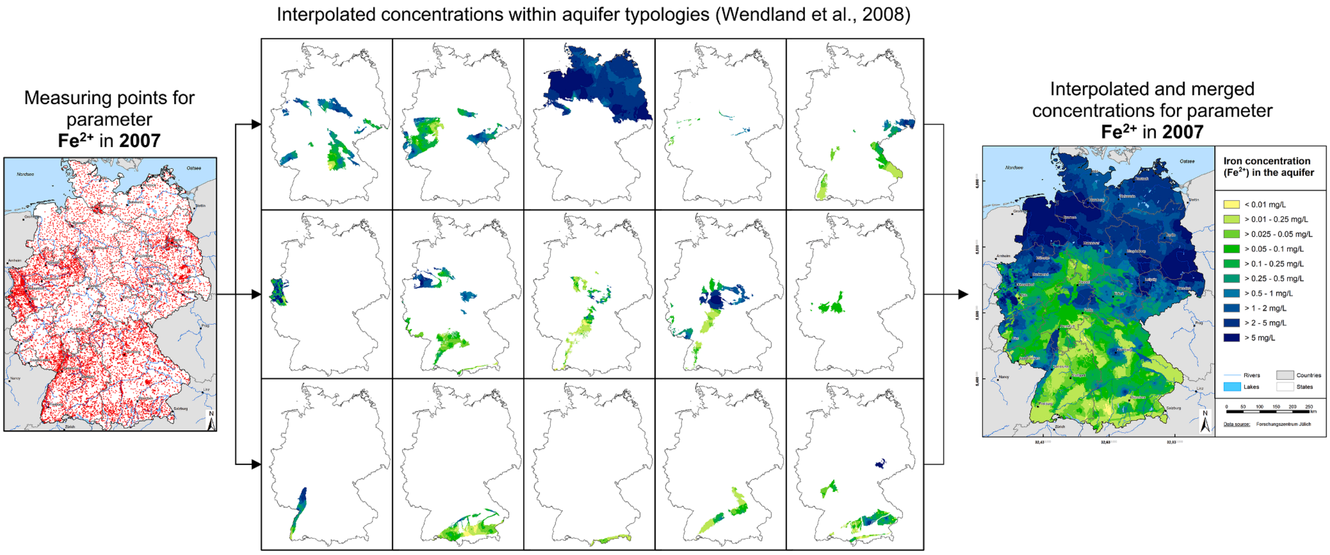

Fig. 4. Exemplary result of the interpolating procedure of groundwater quality parameters for Fe^{2+} measurements in 2007.

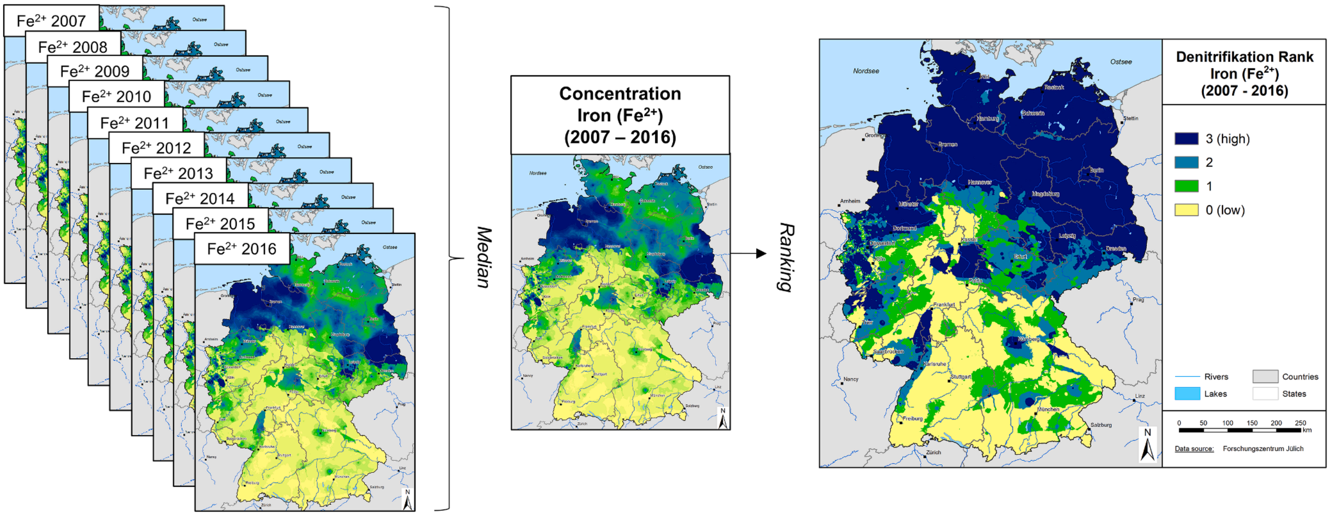

Fig. 5. Exemplary result of the procedure for median averaging from 10 interpolated yearly Fe^{2+} concentrations (2007 – 2016) and successive ranking according to the redox indication classes specified in Table 1.

half-lives of 10 to 40 years. As Fig. 7 indicates groundwater in some unconsolidated rock areas (e.g. the fluviatile sand and gravel aquifers in the Upper Rhine Graben) as well as in some bedrock areas (e.g. the Devonian shales in the Rhenish Slate Mountains) display redox indication class values between 1 and 2. In order to consider the intermediate nitrate degradation conditions in groundwater, half-life times of 2 to 8 years were assigned to this range. Nitrate degradation in groundwater of up to 30 years and more are modeled for the consolidated rock regions in Germany and half-life times of nitrate degradation in groundwater of two years and less in parts of the North German Lowlands, where the redox indication classes of all redox parameters (Fig. 6) showed reduced aquifer conditions.

5.3. Plausibility assessment of the derived denitrification

Fig. 8 compares the observed nitrate denitrified by the N_2/Ar method at the 820 selected stations and the modeled nitrate denitrified at the corresponding locations. The top panel depicts the results as a confusion matrix and histograms, while the lower panel shows how the results vary spatially. Four classes of nitrate degradation were formed to allow this classification: 0–25 %, 25–50 %, 50–75 % and 75–100 % degradation of the initial nitrate in groundwater. According to this classification, 44 % of the measuring points show good agreement, i.e. simulated and measured nitrate degradation fall into the same class, another 26 % show a fair agreement, meaning a deviation of one class.

The lower histogram in Fig. 8 (top) illustrates that for31% of the measurement locations, the modeled denitrification is higher than the observed values, while for 24 % the modeled values are lower than the observed nitrate denitrified in the groundwater. The mean difference between modeled and observed nitrate degradation (bias) is 4 %. The normally distributed differences between modeled and observed data allows an assessment of the limits of agreement derived from a Bland-Altman plot (Bland and Altman, 1986). The upper/lower limits (mean of the difference between modeled and observed nitrate degradation plus/minus the 1.96-fold standard deviation of the respective difference) are 86 % / −78 %, which reflects a high statistical variance of the calculated differences of modeled to the observed N_2/Ar nitrate degradation. Fig. 8 (bottom) illustrates the spatial distributionof N_2/Ar stations with good or poor agreement with no apparent region where the model performance is substantially better or worse than the average

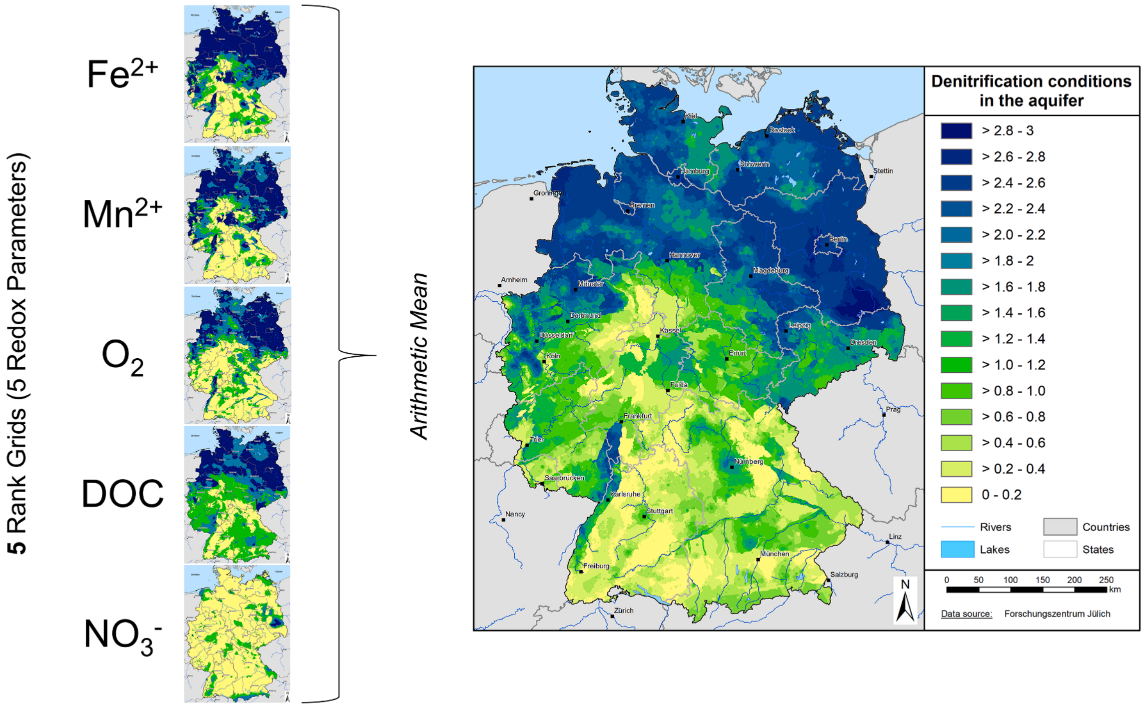

Fig. 6. Derived Denitrification conditions in groundwater indicated as values from 0 (low) to 3 (high) (right) resulting from averaging the rank grids of the redox-sensitive parameters (left).

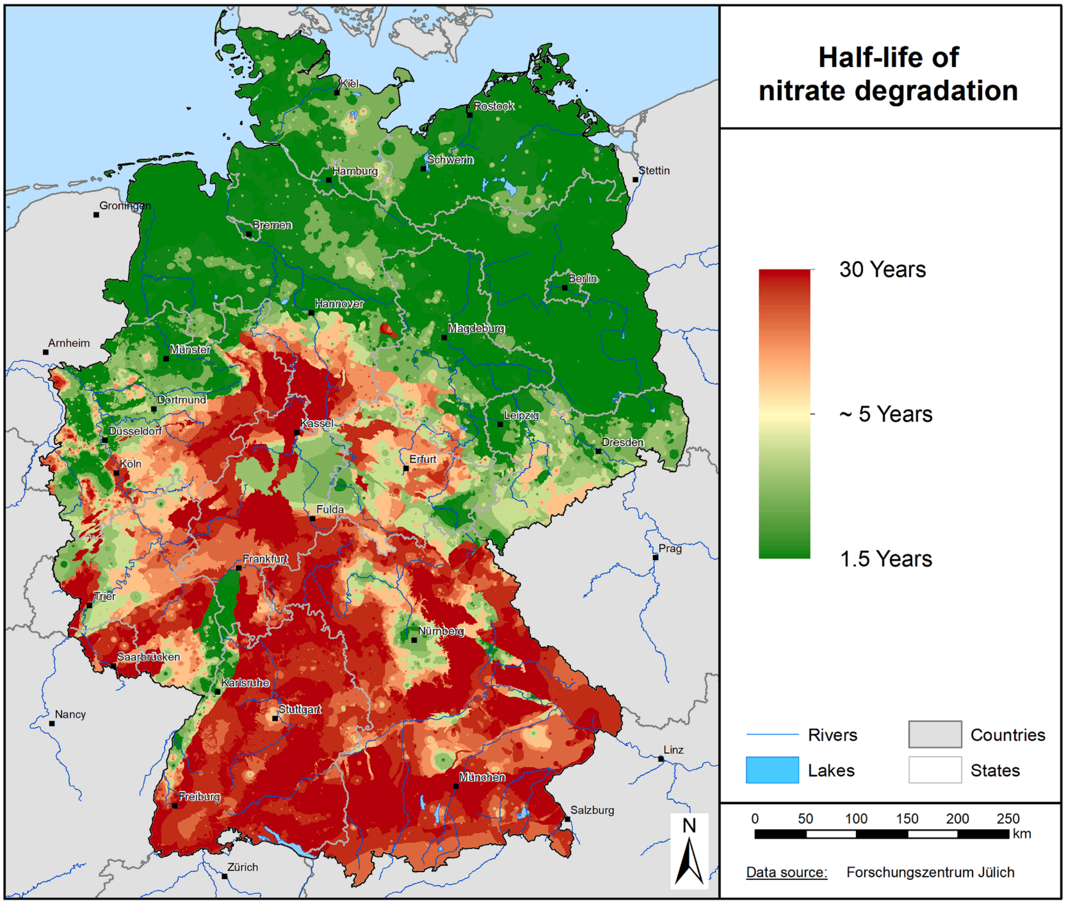

Fig. 7. Regionalized half-life time of nitrate degradation in groundwater.

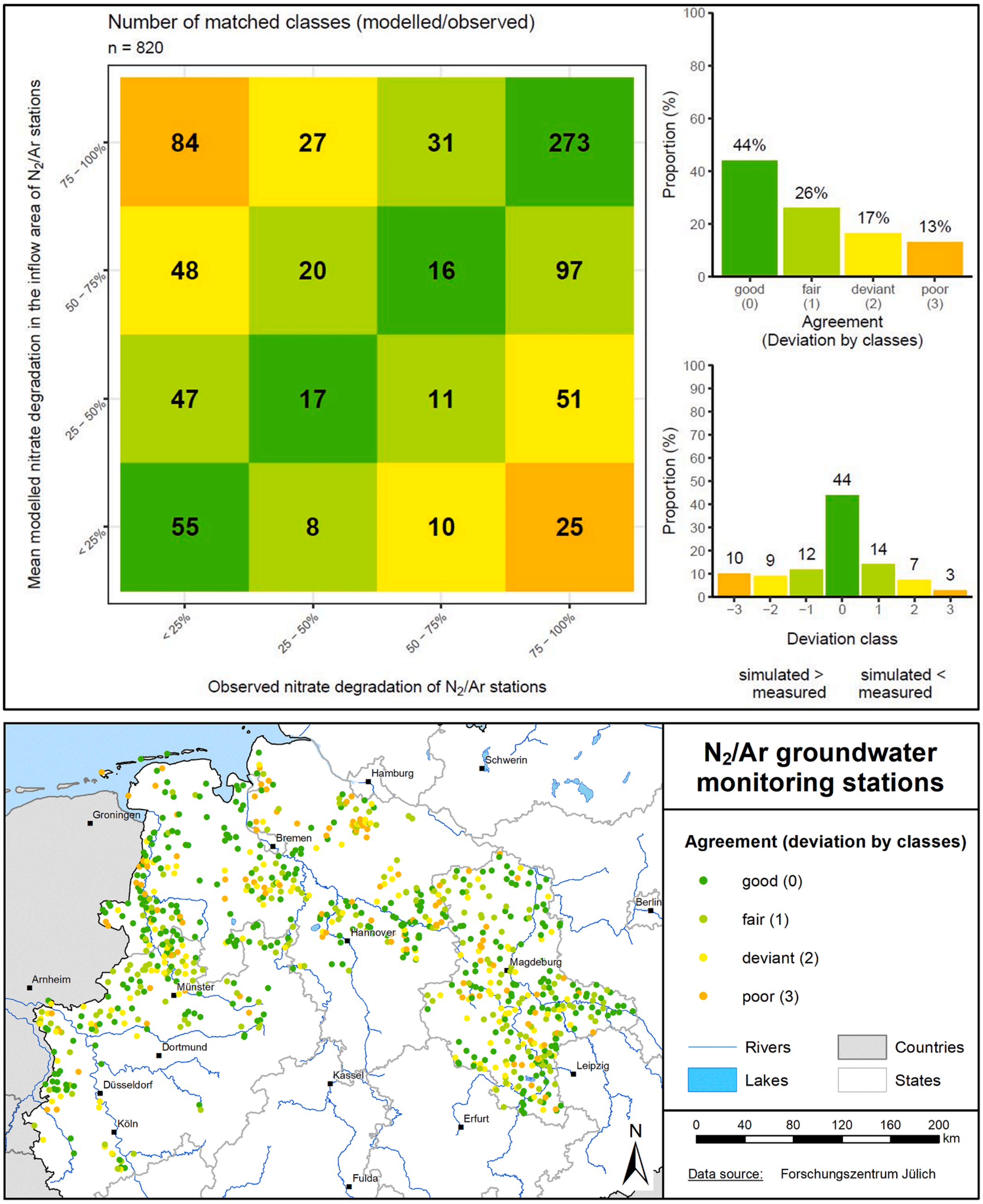

Fig. 8. Comparison of the modeled nitrate degradation in groundwater in the inflow area of N_2/Ar monitoring wells with the nitrate degradation determined by the N_2/Ar method (top) and location of the N_2/Ar monitoring wells displaying the agreement of modeled and observed values as deviation by classes (bottom).

performance over the entire evaluation area.

6. Discussion

We used five hydrochemical groundwater parameters to derive estimates of denitrification conditions in groundwater: oxygen, nitrate, bivalent iron, bivalent manganese and DOC. Numerous studies have demonstrated that these parameters are redox-sensitive for various concentration ranges, thus impacting the denitrification conditions in groundwater (see Chapter 2.2). We did not select pH because denitrifiers are active over the whole pH range typically found in groundwater (see Chapter 2.2.6), while we did not select redox potential because of the influences of external factors on measurements and thus the limited reliability of the measured values as well as the fact that it is often not determined through groundwater sampling (see Chapter 2.2.7). The resulting map of denitrification conditions shows a similar spatial distribution throughout Germany compared to Knoll et al. (2020), who used only the parameters of bivalent iron and oxygen for estimating redox conditions. However, there are regional differences such as lower denitrification potential in a central northern area and higher potential in a central eastern pocket in our map, which are assumed to be primarily due to inclusion of additional redox-sensitive parameters bivalent manganese, DOC and nitrate. In our rank-based approach, all five hydrochemical parameters are considered to be of equal importance to the denitrification conditions in groundwater, which is why none of the parameters are weighted. In our results, it is evident that the spatial distributions of denitrification class of bivalent iron and bivalent manganese are similar. Thus, if applying this methodology for further studies to a different region where one of these two parameters might not have been measured (e.g. Mn^{2+}), it could be substituted with a doubleweighted parameter (e.g. Fe^{2+}) without substantially affecting the final assessment of denitrification conditions in groundwater. To a certain degree, but with higher expected uncertainties, this is also the case for oxygen or DOC, which shows a partly similar spatial distribution of denitrification classes, at least within Germany. It is also conceivable to expand the methodology to include other redox-sensitive parameters such as redox potential and pH, provided there is a reliable database available.

Through the integration of the derived denitrification conditions with information on first-order reaction kinetics, we were able to quantify denitrification rates in our model. The application of our methodology requires input information on the nitrate inputs, flow direction of groundwater as well as flow velocity of groundwater, which are subject to various uncertainties that are discussed in the paragraph after the next.

The modeled denitrification rates in groundwater could mostly be confirmed by N_2/Ar measurements available from parts of central/north Germany. Our results suggest that both the reliability of the denitrification conditions and the associated reaction constants of denitrification in groundwater have been confirmed, which contradicts the conclusion of Kludt (2020), who concluded that degradation kinetics are not related to degradation potential, i.e., the concentrations of the redox parameters described above. Most of the monitoring stations where a good agreement between modeled and observed values was obtained were for the nitrate degradation class 75 – 100 %. Hence, the regions for which the denitrification conditions in groundwater were close to the values of 3 appear to have been represented very well in the model. Also, there was no apparent systematic overestimation or underestimation of the nitrate denitrified in the groundwater. Furthermore, the normally distributed differences between modeled and observed data show that the upper/lower limits reflect a high statistical variance of the calculated differences of modeled to the observed N_2/Ar nitrate degradation. The spatial distribution of the results for the N_2/Ar analysis demonstrate that there is no noticeable spatial clustering of N_2/Ar stations with good or poor agreement. 159 of the 1,259 N_2/Ar monitoring sites were not included in the plausibility assessment due to a very low initial nitrate concentration. For monitoring sites showingvery low initial nitrate concentration, there still exists the possibility that the soils occurring in the groundwater inflow areas of the monitoring sites are influenced by groundwater and contain a high proportion of organic matter. In such soils, high denitrification rates can be achieved (Eisele et al., 2008; Schilling, 2006; Well et al., 2005; Wienhaus et al., 2008), so that nitrate can be almost completely degraded in soil. In addition, at these sites, the denitrification processes in soil and groundwater cannot be easily separated. Notwithstanding the fact that for such monitoring sites the calculation of nitrate degradation is more complicated (Blicher-Mathiesen et al., 1998) with the N_2/Ar method, good denitrification conditions (Fig. 6) and low half-lives of denitrification (Fig. 7) in groundwater can prevail. Thus, the exclusion of those N_2/Ar monitoring sites may prevent a plausibility assessment at the very sites that are particularly important for understanding denitrification in groundwater.

The observed deviations may reflect small-scale heterogeneities not accounted for in the input data of the WEKU model. For example, they originate from the N inputs to groundwater related to the intensity of land management (fertilization rate) or to the crops grown. Moreover deviations may result from the calculated travel times in groundwater and the inflow area of the groundwater wells both derived from the modeled simplified groundwater surface and travel times derived by mean assumed values of hydraulic conductivity. Lastly the accuracy of derived denitrification conditions in groundwater is, among other variables, dependent on the density of monitoring wells. In spite of uncertainties in our model results the findings are similar to those reported in Eschenbach et al. (2018) who also compared modeled nitrate inputs into groundwater (DENUZ-Model) to nitrate inputs derived from N_2/Ar measurements. Eschenbach et al. (2018) showed that simulated and measured nitrate degradation in the groundwater can differ substantially at the level of a single groundwater monitoring wells, thus underlining the necessity of analyzing large datasets of N_2/Ar measurements to assess the plausibility of modeled denitrification conditions in aquifers.

There is potential to improve individual parts of the model and observed data and therefore decrease uncertainties in plausibility assessment:

- One possibility to improve the accuracy of the rank-based map of denitrification conditions through the inclusion of more groundwater quality wells. The spatial representativity of the derived denitrification conditions in groundwater strongly depends on the density of measuring points over all aquifer typologies. For the case study of Germany, the station density varies regionally, which affects the representativity of the derived denitrification conditions in groundwater. To overcome this limitation, a homogenization, and in some regions also a densification, of the groundwater monitoring network in Germany is recommended. This would enhance the validity of the interpolation model while also enabling the use of smaller scale aquifer typology regions to provide a more realistic delineation of the subsurface on a regional scale.
- Also, the map of denitrification conditions can be improved by conducting a detailed analysis of the effect of filter depth of groundwater quality wells on the concentration of the redox-sensitive parameters and integrate this information into the interpolation model.
- Uncertainties in modeling the groundwater surface, which impact both the travel time to the wells and the inflow area of the wells, could be reduced by using more advanced process-based groundwater flow models.
- The *N*-input into the groundwater modeled by the nutrient model DENUZ could be improved by further enhancing the two decisive input data sets of groundwater recharge modelled by the water balance model and the N balance surpluses targeting higher resolution modeling (e.g. farm scale).
- Nitrate degradation deduced from N_2/Ar measurements could be improved, for example by extending the N_2/Ar measurements over multiple years and therefore confirming the existing single or at maximum twice done analysis to exclude time-dependent variations or measurement errors.

7. Summary

We developed and applied a methodology to generate spatially continuous maps of the denitrification potential in aquifers based on the parameters collected in standardized groundwater monitoring program. The derived Germany-wide denitrification conditions in groundwater show that extensive regions of reduced (denitrifying) groundwater prevail in the sand and gravel aquifers of the North German Lowlands and oxidized (non-denitrifying) groundwater conditions in all bedrock regions of the low mountain ranges. There is a gradual transition from groundwater showing non-nitrate-degrading conditions (values close to 0) to groundwater showing nitrate-degrading conditions (values close to 3).

The assumed relationship between denitrification conditions and denitrification kinetics in groundwater was confirmed through the plausibility assessment, where we compared our denitrification rates modeled with the WEKU model against the denitrification rates determined with the N_2/Ar measurements in groundwater based on 820 measurement stations from the German federal states of North-Rhine-Westphalia, Lower Saxony and Saxony-Anhalt.

In a more general sense, the derivation of denitrification conditions in groundwater is not only important for modeling reliable denitrification rates in groundwater but also for explaining discrepancies between high nitrate outputs from soil and low measured nitrate concentrations in groundwater and surface waters.

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CRediT authorship contribution statement

Tim Wolters: Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Visualization, Conceptualization, Writing – original draft, Writing – review & editing. **Thomas Bach:** Resources, Data curation. **Michael Eisele:** Resources, Data curation, Writing – review & editing. **Wolfram Eschenbach:** Resources, Data curation, Writing – review & editing. **Ralf Kunkel:** Methodology, Software, Validation, Resources, Writing – review & editing. **Ian McNamara:** Conceptualization, Writing – original draft, Writing – review & editing. **Reinhard Well:** Resources, Data curation. **Frank Wendland:** Conceptualization, Methodology, Validation, Investigation, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition.

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

The authors do not have permission to share data.

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