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Predicting long-term denitrification capacity of sandy aquifers from incubation experiments and sediment properties

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Abstract

Knowledge about the spatial variability of denitrification rates and the lifetime of denitrification in nitrate-contaminated aquifers is crucial to predict the development of groundwater quality. Therefore, regression models were derived to estimate the measured denitrification capacity of incubated aquifer sediments from initial denitrification rates and several sediment parameters, namely total sulphur, total organic carbon, extractable sulfate, extractable dissolved organic carbon, hot water soluble organic carbon and potassium permanganate labile organic carbon.

For this purpose, we incubated aquifer material from two sandy Pleistocene aquifers in Northern Germany under anaerobic conditions in the laboratory using the ^{15}N tracer technique. The measured long-term denitrification capacities ranged from 0.18 to $56.2 \text{ mg N kg}^{-1} \text{ yr}^{-1}$. The laboratory incubations exhibited high differences between non-sulphidic and sulphidic aquifer material in both aquifers with respect to all investigated sediment parameters. Denitrification rates and the estimated lifetime of denitrification were higher in the sulphidic samples. Denitrification capacity measured during one year of incubation (D_{cap}) was predictable from sediment variables within a range of uncertainty of 0.5 to 2 (calculated D_{cap} /measured D_{cap}) for aquifer material with a $D_{\text{cap}} > 20 \text{ mg N kg}^{-1} \text{ yr}^{-1}$. Predictions were poor for samples with lower D_{cap} like samples from the NO_3^- -bearing groundwater zone, which includes the non-sulphidic samples, from the upper part of both aquifers where D_{cap} is not sufficient to protect groundwater from anthropogenic NO_3^- input. Calculation of D_{cap} from initial denitrification rates was only successful for samples from the NO_3^- -bearing zone, whereas a lag-phase of denitrification in samples from deeper zones of NO_3^- free groundwater caused imprecise predictions.

Our results thus show that D_{cap} of sandy Pleistocene aquifers can be predicted using a combination of short-term incubation and analysis of sediment parameters. Moreover, the protective lifetime of denitrification sufficient to remove NO_3^- from groundwater

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in the investigated aquifers is limited which demonstrates the need to minimize anthropogenic NO_3^- input.

1 Introduction

Denitrification, the microbial mediated reduction of nitrate (NO_3^-) and nitrite (NO_2^-) to the nitrogen gasses nitric oxide (NO), nitrous oxide (N_2O) and dinitrogen (N_2) is important to water quality and chemistry at landscape, regional and global scales (Groffman et al., 2006). Since 1860 the inputs of reactive nitrogen (Nr)¹ to terrestrial ecosystems have increased from 262 to 389 Tg N yr⁻¹ (Galloway et al., 2004). The production of reactive nitrogen via the Haber-Bosch process contributed approximately with 100 Tg N yr⁻¹ to this tremendous increase. In the European Union diffuse emissions of Nr range from 3 to $>30 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ from which 51 to 85 % are derived from agriculture (Bouraoui et al., 2009). Diffuse Nr emissions from the agricultural sector are therefore the dominant source of NO_3^- fluxes to aquatic systems which leads to the questions, how rates of denitrification will respond to Nr loading (Seitzinger et al., 2006) and where and how long denitrification in aquifers can remediate the anthropogenic NO_3^- pollution of groundwater (Kölle et al., 1985).

NO_3^- pollution of groundwater has become a significant problem due to eutrophication of water bodies (Vitousek et al., 1997) and potential health risks from NO_3^- in drinking water. The latter causes increasing costs for keeping the standard for NO_3^- in drinking water ($<50 \text{ mg l}^{-1}$, Drinking Water Directive 98/83/EC) (Dalton and Brand-Hardy, 2003; Defra, 2006). Therefore, knowledge about the denitrification capacity of aquifers is highly needed.

¹ The term reactive nitrogen is used in this work in accordance to Galloway et al. (2004) and includes all biologically or chemically active N compounds like reduced forms (e.g., NH_3 , NH_4^+), oxidized forms (e.g., NO_x , HNO_3 , N_2O , NO_3^-) and organic compounds (e.g., urea, amines, proteins ...).

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Denitrification in groundwater is mainly depending on the amount and microbial availability of reduced compounds in the aquifers, capable to support denitrification and is of a high spatial variability, ranging from 0 to 100 % of the NO_3^- input (Seitzinger et al., 2006). The main constituents of reduced compounds acting as electron donor during denitrification are organic carbon (heterotrophic denitrification pathway), reduced iron and reduced sulphur compounds (autotrophic denitrification pathway). Iron sulphides are known to be an important electron donor for autotrophic denitrification (Kölle et al., 1985), recently Korom et al. (2012) indicated that non-pyritic ferrous iron might play a more important role for denitrification than considered up to now. They assume that ferrous iron from amphibols contributed to denitrification with 2–43 % in a glaciofluvial shallow aquifer in North Dakota.

Denitrification in groundwater can be a very slow to fast process. Frind et al. (1990) reported that autotrophic denitrification has a half-life of 1 to 2 yr in the deeper zone (5 to 10 m below soil surface) of the well investigated Fuhrberger Feld aquifer (FFA). Contrary to the high denitrification rates in deeper reduced parts of this aquifer (autotrophic denitrification zone) Weymann et al. (2010) reported very low denitrification rates with values as low as $4 \mu\text{g N kg}^{-1} \text{d}^{-1}$ in the surface near groundwater (heterotrophic denitrification zone) of the same aquifer. Denitrification rates in the heterotrophic zone were one to two orders of magnitude lower than in its deeper parts and altogether too low to remove NO_3^- from groundwater.

While there are numerous laboratory incubation studies evaluating denitrification rates of aquifer sediments, there are only few studies reporting long-term denitrification capacity and/or the stock of reactive compounds capable to support denitrification in the investigated aquifer sediments (Kölle et al., 1985; Houben, 2000; Mehranfar, 2003; Weymann et al., 2010; Well et al., 2005). Even less investigations tried to develop stochastic models to estimate the denitrification capacity from independent sediment variables (Konrad, 2007; Well et al., 2005). Mehranfar (2003) and Konrad (2007) estimated the availability of a given stock of reduced compounds within sediments during long-term incubation experiments, showing that approximately 5 to 50 % of sulphides

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were available for denitrification during incubation. However, in both studies incubation time was insufficient for complete exhaustion of reductants within the experiments.

Since laboratory investigations of denitrification rates in and denitrification capacities of aquifer material are time consuming and expensive, in situ measurements are helpful to increase knowledge about the spatial distribution of denitrification in aquifers. In situ denitrification rates can be derived from concentration gradients (Tesoriero and Puckett, 2011), in situ mesocosms (Korom et al., 2012) and from push-pull type ^{15}N -tracer tests (Addy et al., 2002; Well and Myrold, 1999). Well et al. (2003) compared in situ and laboratory measurements of denitrification rates in water saturated hydro-morphic soils and showed that both methods were over all in good agreement. Konrad (2007) proposed to estimate long-term denitrification capacity of aquifers from in situ push-pull tests as an alternative to costly drilling of aquifer samples with subsequent long-term incubations. A good correlation between in situ denitrification rates and long-term denitrification capacity based on a small number of comparisons was reported (Konrad, 2007), but the data-set was too small to derive robust transfer functions.

Since the oxidation of reduced compounds in aquifers is an irreversible process, the question arises, how fast ongoing NO_3^- input will exhaust denitrification capacity of aquifers and to which extent this may lead to increasing NO_3^- concentrations. Two studies attempted to answer this. Kölle et al. (1985) calculated the maximum lifetime of autotrophic denitrification in the FFA of about 1000 yr by a mass balance approach. Houben (2000) modelled the depth shift of the denitrification front in a sandy aquifer in Western Germany giving a progress rate of approximately 0.03 myr^{-1} .

Overall, there is limited information on long-term denitrification capacity of aquifer sediments because there are few direct measurements and because predictions based on stochastic models are hampered by the lack of suitable data sets. Therefore, knowledge about the spatial distribution of denitrification rates is highly demanded (Rivett et al., 2008). To progress knowledge in this field, we combine established methods with the testing of new concepts. Our goals are (a) to quantify exhaustibility of long-term denitrification capacity in aquifers, (b) to investigate controlling factors and derive

predictive models, and (c) to check if long-term denitrification capacity can be derived from actual in situ rates of denitrification measurable using push-pull tests at ground-water monitoring wells. Here we present a study to tackle (a) and (b). The specific objectives are (i) to measure denitrification during long-term anaerobic incubation of 5 sediment material from two aquifers, (ii) to estimate the total stock of reactive compounds in these samples and their availability for denitrification as well as influencing sediment parameters, (iii) to develop regression models to estimate long-term denitrification capacity from initial denitrification rates and from sediment properties and (iv) to estimate minimal lifetime of denitrification in the investigated aquifer material.

10 2 Materials and methods

2.1 Study sites

Aquifer material was collected in the Fuhrberger Feld aquifer (FFA) and the Großenketten aquifer (GKA), two drinking water catchment areas in Northern Germany. The FFA is situated about 30 km NE of the city of Hannover and the GKA about 15 30 km SW of the city of Bremen. Both aquifers consist of carbonate free, Quaternary sands and the GKA additionally of carbonate free marine sands (Pliocene). The thickness of the FFA and GKA is 20 to 40 m and 60 to 100 m, respectively. Both aquifers are unconfined and contain unevenly distributed amounts of microbial available sulphides and organic carbon. Intense agricultural land use leads to considerable nitrate inputs to 20 the groundwater of both aquifers (Böttcher et al., 1990; van Berk et al., 2005). Groundwater recharge has been estimated 250 mm yr^{-1} in the FFA (Wessolek et al., 1985) and $200 \text{ to } 300 \text{ mm yr}^{-1}$ in the GKA (Schuchert, 2007).

Evidence of an intense ongoing denitrification within the FFA is given by nitrate and 25 redox gradients (Böttcher et al., 1992) as well as excess- N_2 measurements (Weymann et al., 2008). The FFA can be divided into two hydro-geochemical zones, the zone of heterotrophic denitrification near the groundwater surface with organic carbon (C_{org})

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as electron donor and a deeper zone of predominantly autotrophic denitrification with pyrite as electron donor (Böttcher et al., 1991, 1992). Detailed information about the FFA is given by Strelbel et al. (1992), Frind et al. (1990) and von der Heide et al. (2008). Extended zones with oxidizing and reducing conditions in the groundwater are also evident in the GKA (van Berk et al., 2005) but their distribution within this aquifer is more complex as in the FFA. The geological structure of the GKA is described in Howar (2005) and Wirth (1990). Intense denitrification is known to occur in the zone of reduced groundwater (van Berk et al., 2005). This was proven by excess-N₂ measurements at monitoring wells within the GKA (Well et al., 2012). But there are no studies on the type of denitrification in this aquifer.

2.2 Sampling procedures

The aquifer material used in this study originated from depths between 3–18 m and 8–68 m below soil surface of the FFA and GKA, respectively.

The aquifer material from the FFA was drilled with a hollow stem auger (OD of 15 205 mm, ID of 106 mm, WELLCO-DRILL, WD 500, Beedenbostel, Germany) and the core samples were immediately transferred into 2 l glass bottles. The remaining headspace within these bottles was filled with deionized water until it overflowed. Then the bottles were sealed airtight with rubber covered steel lids. Aquifer material from the GKA was drilled by percussion core drilling. The aquifer samples were collected with 20 a double core barrel with an inner PVC liner (OD 95.8 mm, ID 63.4 mm, HWL(HQ) Wireline core barrel, COMPDRILL Bohrausrüstungen GmbH, Untereisesheim, Germany). After sampling, the liner was removed from the core barrel and sealed airtight at both ends with PVC lids. In the laboratory, the aquifer material from the PVC liner was transferred into glass bottles as described above. The aquifer samples were stored at 10 °C 25 (approximately the mean groundwater temperature in both aquifers) in the dark. After sampling of aquifer material, groundwater monitoring wells and multilevel wells were installed in the borings.

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2.3 Laboratory incubations

2.3.1 Standard treatment

Anaerobic incubations were conducted to measure the denitrification capacity and the denitrification rates of the investigated aquifer material as described by Weymann et al. (2010). In total, 41 samples from both aquifers collected between 2 to 68 m below soil surface were incubated. From each sample, 3 to 4 replicates of 300 g fresh aquifer material were filled in 1125 ml transfusion bottles. 300 ml ^{15}N labelled KNO_3 solution ($200 \text{ mg l}^{-1} \text{ KNO}_3$ in deionized water; 60 % ^{15}N) was added to each transfusion bottle and then the bottles were sealed airtight with rubber septa and aluminium screw caps. The mixture of the labelled KNO_3 solution and pore water of the aquifer samples is referred to as batch solution below. The headspace of each transfusion bottle was evacuated for 5 min and then flushed with pure N_2 . This procedure was repeated 5 times to ensure anaerobic conditions within the bottles. Samples were incubated for one year in the dark at 10 °C.

The water content of the investigated aquifer material was determined gravimetrically using parallels of the incubated material. The dry weight, the volume of the incubated sediment (assuming a particle density of 2.65 g cm^{-3}), the liquid volume and the headspace volume were calculated for each replicate independently. Samples of the headspace gas and the supernatant batch solution were taken at days 1, 2, 7, 84, 168 and 365 of incubation. The transfusion bottles were shaken on a horizontal shaker at 10 °C for 3 h prior to sampling to equilibrate headspace gasses with the dissolved gasses in the batch solutions. For the gas sampling, 13 ml headspace gas were extracted with a syringe and transferred to evacuated 12 ml sample vials (Exetainer® Labco, High Wycombe, UK). Subsequently, 20 ml of the supernatant solution were sampled with a syringe and transferred into a PE bottle and frozen until analysis. To maintain atmospheric pressure within the transfusion bottles, 13 ml pure N_2 und 20 ml of O_2 free ^{15}N labelled KNO_3 solution were re-injected into every transfusion bottle

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after sampling. The ^{15}N -labelled KNO_3 solution was stored in a glass bottle, which was sealed air tight with a rubber stopper. Prior to re-injection of the KNO_3 solution into the transfusion bottles, the solution was purged with pure N_2 through a steel capillary for 1 h to remove dissolved O_2 . The headspace in the glass bottle was sampled to check O_2 contamination and was always found to be in the range of O_2 signals of blank samples (N_2 injected into evacuated 12 ml sample vials).

2.3.2 Intensive treatment

A modified incubation treatment was conducted for aquifer samples with high content of C_{org} and sulphides, to increase the proportion of reduced compounds that are oxidized during incubation. 30 g aquifer material and 270 g quartz sand were filled in transfusion bottles and prepared for anaerobic incubations as described above for the "standard" treatment. The incubation temperature was 20 °C and samples were permanently homogenized on a rotary shaker in the dark. In total, 9 aquifer samples were selected from the FFA and GKA and incubated in 4 replications. Additionally, 4 transfusion bottles were filled only with the pure quartz sand to check for the possible denitrification activity of this material, which was found to be negligible.

2.4 Analytical techniques

The particle sizes distribution in the aquifer sediments was determined by wet sieving. The silt and clay fractions were determined by sedimentation following the Atterberg-method (Schlichting et al., 1995). Contents of total sulphur (total-S), total nitrogen (total-N) and total organic carbon (C_{org}) of the carbonate free aquifer sediments were analysed with an elemental analyser (vario EL III, ELEMENTAR ANALYSESYSTEME, Hanau, Germany).

For hot water soluble organic carbon (C_{hws}) 10 g aquifer material and 50 ml deionized water were boiled for 1 h and then filtrated (Behm, 1988). Cold water extracts where used for the determination of extractable dissolved organic carbon (DOC_{extr})

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and extractable sulphate ($\text{SO}_4^{2-}_{\text{extr}}$). C_{hws} and DOC_{extr} in the extracts were measured with a total carbon analyser (TOC 5050, Shimadsu, Kyoto, Japan). To measure the fraction of KMnO_4 labile organic carbon (C_l) 15 g aquifer material and 25 ml 0.06 M KMnO_4 solution were shaken on a rotating shaker for 24 h and then centrifuged by 865 RCF (Konrad, 2007). 1 ml of the supernatant was sampled and diluted in 100 ml dionized water. C_l was then determined as the decolourization of the KMnO_4 solution by means of a photometer (SPECORD 40, Analytic Jena, Jena, Germany). NO_3^- , NO_2^- and NH_4^+ concentrations were determined photometrically in a continuous flow analyser (Skalar, Erkelenz, Germany). For the determination of SO_4^{2-} concentrations in the batch solutions and SO_4^{2-} extracts, a defined amount of BaCl_2 solution was added in excess to SO_4^{2-} to the samples and SO_4^{2-} precipitated as BaSO_4^{2-} . The original SO_4^{2-} concentration was then analysed by potentiometric back-titration of the excess Ba_2^+ ions remaining in the solution using EDTA as titrant. Possible interfering metal cations were removed from the samples prior to this analysis by cation exchange.

The major cations in the batch solution (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Mn_4^+ , Fe_3^+ and Al_3^+) were measured by means of Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES, Spectro Analytical Instruments, Kleve, Germany) after stabilizing an aliquot of the batch solution samples with 10 % HNO_3 .

N_2O was measured using a gas chromatograph (Fisons GC8000, Milan, Italy) equipped with an electronic capture detector as described previously by Weymann et al. (2009). O_2 was analysed with a gas chromatograph equipped with a thermal conductivity detector (Fractovap 400, CARLO ERBA, Milan, Italy) described in Weymann et al. (2010).

The ^{15}N analysis of denitrified ($\text{N}_2 + \text{N}_2\text{O}$) was carried out by a gas chromatograph (GC) coupled to an isotope ratio mass spectrometer (IRMS) at the Centre for Stable Isotope Research and Analysis in Göttingen, Germany within two weeks after sampling, following the method described in Well et al. (2003). The concentrations of ^{15}N labelled denitrified N_2 and N_2O in the gas samples were calculated in the same way as

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described in detail by Well and Myrold (1999) and Well et al. (2003). From the obtained molar concentrations of denitrified N_2 and N_2O in the gas samples, which are equal to the molar concentrations in the headspace of the transfusion bottles, the dissolved N_2 and N_2O concentrations in the batch solutions were calculated. This was done according to Henry's law using the solubilities for N_2 and N_2O at 10 °C given by Weiss (1970) and Weiss and Price (1980). The detection limit of ^{15}N analysis was calculated as the minimum amount of ^{15}N labelled denitrification derived ($\text{N}_2 + \text{N}_2\text{O}$) mixed with the given background of headspace N_2 of natural ^{15}N abundance necessary to increase the measured $^{29}\text{N}_2/^{28}\text{N}_2$ ratio to fulfil the following equation:

$$^{10} r_{\text{sa}} - r_{\text{st}} \geq 3 \times \text{s.d.} r_{\text{st}} \quad (1)$$

where r_{sa} and r_{st} are the $^{29}\text{N}_2/^{28}\text{N}_2$ ratios in sample and standard, respectively and $\text{s.d.} r_{\text{st}}$ is the standard deviation of repeated r_{st} measurements. The r_{st} values were analysed with IRMS by measuring repeated air samples. Under the experimental conditions, the detection limit for the amount of denitrified ^{15}N labelled ($\text{N}_2 + \text{N}_2\text{O}$) was 15 to 25 $\mu\text{g N kg}^{-1}$.

Dissolved oxygen, pH and electrical conductivity (pH/Oxi 340i and pH/Cond 340i, WTW Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, Germany) were measured in the groundwater from the installed groundwater monitoring wells.

2.5 Calculated parameters

20 The following parameters describing the denitrification dynamics during anaerobic incubation were calculated from the measurements described above. Denitrification rates $D_r(X)$ were calculated as the cumulative amount of denitrification products formed until the day of sampling divided by the duration of incubation until sampling ($\text{mg N kg}^{-1} \text{d}^{-1}$), with X as the day of sampling. We calculated denitrification rates for day 7, 84, 168 and 25 365 of incubation, $D_r(7)$, $D_r(84)$, $D_r(168)$ and $D_r(365)$, respectively. $D_r(7)$ is also referred to as the initial denitrification rate. The denitrification capacity (D_{cap}) is the cumulative

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amount of denitrification products per kg dry weight of incubated aquifer material at the end of one year of incubation ($\text{mg N kg}^{-1} \text{yr}^{-1}$). $D_r(365)$ multiplied by 365 d equals D_{cap} , so we refer only to D_{cap} below. The sulphate formation capacity (SFC) (Kölle et al., 1985) was derived from the measured increase of SO_4^{2-} concentrations in the batch solution between the first sampling (day 1) and the end of incubation (day 365). To correct the SFC value for dissolution of possible SO_4^{2-} -minerals and/or SO_4^{2-} from the pore water of the incubated aquifer material we subtracted the SO_4^{2-} concentrations in the batch solution after two days of incubation from the finally SO_4^{2-} concentration after one year. The stock of reactive compounds (SRC) was estimated from total-S and C_{org} data. For simplicity it was assumed that C_{org} corresponds to an organic substance with the formula CH_2O (Korom, 1991; Trudell et al., 1986) and that all sulphur was in the form of pyrite (FeS_2) (see section 4.3.1). C_{org} and total-S values were converted into N equivalents (mg N kg^{-1}) according their potential ability to reduce NO_3^- to N_2 . C_{org} was converted according to Eq. (4) given in Korom (1991) and total-S values (in form of pyrite) according to Eqs. (5) and (6) given in Kölle et al. (1983). The fraction of SRC which is available for denitrification during incubation (aF_{SRC}) (%) was calculated as the ratio of the measured D_{cap} to the SRC of the incubated aquifer material. The share of total-S values contributing to the aF_{SRC} was calculated from the measured SFC during incubation. The remaining portion of the aF_{SRC} as assigned to microbial available C_{org} compounds in the aquifer samples.

The minimum lifetime of denitrification (emLoD) was estimated as follows:

$$\text{emLoD} = \frac{A_{\text{dw}} \cdot (\text{SRC} \cdot aF_{\text{SRC}} \cdot 0.01)}{\text{nitrate input}} \quad [\text{yr m}^{-3}] \quad (2)$$

where the dry weight of 1 m^3 aquifer material (A_{dw}) (kg m^{-3}) is multiplied with the fraction of its SRC (mg N kg^{-1}) content available for denitrification during one year of incubation. This value is then divided by the nitrate input ($\text{mg NO}_3^- \text{Nm}^{-2} \text{yr}^{-1}$) giving the estimated minimal lifetime of denitrification for one m^3 of aquifer material. To calculate

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A_{dw} a porosity of 35 % and an average density of the solid phase of 2.65 g cm^{-3} of the aquifer material was assumed, giving an A_{dw} of 1722.5 kg m^{-3} . Furthermore, an average aF_{SRC} of 5 % was used to calculate emLoD (see Sect. 4.4). The NO_3^- input to the aquifer coming with the groundwater recharge was assumed from literature data on N-leaching. Köhler et al. (2006) measured mean NO_3^- concentrations in the groundwater recharge under arable sandy soils between 40 and $200 \text{ mg NO}_3^- \text{ l}^{-1}$. For a conservative estimate of emLoD we use the maximum value $200 \text{ mg NO}_3^- \text{ l}^{-1}$. This value gives a nitrate input of $11.3 \text{ g NO}_3^- \text{-Nm}^{-2} \text{ yr}^{-1}$ ($= 6.6 \text{ mg NO}_3^- \text{-N kg}^{-1} \text{ yr}^{-1}$) to the aquifer under condition of a groundwater recharge rate of about 250 mm yr^{-1} as reported for the GKA and FFA by Schuchert (2007) and Renger et al. (1986), respectively.

2.6 Statistical analysis and modelling

Statistical analysis and modelling was performed with WinSTAT for MS Excel Version 2000.1 (R. Fitch Software, Bad Krozingen, Germany). Differences between partial datasets were considered significant at the $P < 0.05$ level (Kruskal-Wallis test (kw), with the null hypothesis that both partial data-sets belong to the same population). Spearman rank correlations (r_s) were used to determine significant correlations between sediment parameters and D_{cap} . Simple and multiple linear regression analysis were performed to evaluate quantitative relations between D_{cap} and the sediment parameters and to predict D_{cap} from these parameters. Simple linear regressions and multiple linear regressions are in the following referred to as simple regression and multiple regressions. Normal distribution of the measured parameters within the different data-sets was tested with the Kolmogorov-Smirnov-Test, normal distribution was assumed at the $P > 0.05$ level, with the null hypothesis that the tested parameter was normal distributed. The uniform distribution of residuals of regressions were checked with scatter plots of residuals vs. independent variables of the respective regression analysis. This was done to ensure homoscedasticity during regression analysis, to ensure that the least-squares method yielded best linear estimators for the modelled parameter.

Experimental data (x) was converted into Box-Cox transformed data ($f^{B-C}(x)$) according to Eq. (3) using different lambda coefficients (λ) to achieve a normal like distribution of experimental data within the different data-sets.

$$f^{B-C}(x) = \frac{x^\lambda - 1}{\lambda} \quad (3)$$

5 Box-Cox transformations were conducted with the statistic software STATISTICA 8 (StatSoft, Tulsa, USA). To use the regression functions to model long-term denitrification, input data have to be transformed according to Eq. (3) with the lambda coefficients given in Table S5 (see the Supplement).

3 Results

10 **3.1 Incubations and independent variables: grouping of aquifer material**

For data analysis, the aquifer material was grouped by locality (FFA and GKA aquifer material). Moreover, chemical sediment properties (non-sulphidic and sulphidic samples) and groundwater redox state at the sample origin (samples from NO_3^- free and

15 NO_3^- bearing groundwater zone of both aquifers were assigned to NO_3^- -free and NO_3^- -bearing sub-groups, respectively) were taken into account for further differentiation. Finally, a transition zone sub-group was defined for samples from the region where sulphides were present, but groundwater still contained NO_3^- . Sulphidic and non-sulphidic samples are distinguished using the sulphate formation capacity (SFC ($\text{mg S kg}^{-1} \text{yr}^{-1}$))

20 of the incubated aquifer material. Samples with $\text{SFC} > 1 \text{ mg SO}_4^{2-} \text{-S kg}^{-1} \text{yr}^{-1}$ were assigned sulphidic. The groundwater at the origin of sulphidic samples had always dissolved O_2 concentrations below $1.5 \text{ mg O}_2 \text{l}^{-1}$. The groundwater at the origin of NO_3^- -free samples was completely anoxic in both investigated aquifers. In our data-set, sub-groups of non-sulphidic and NO_3^- -bearing as well as sulphidic and NO_3^- -free samples

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were almost identical (Tables S1 and S2 in the Supplement). Moreover, statistically significant differences were only found in D_{cap} with higher values for NO_3^- -bearing in comparison to non-sulphidic samples. NO_3^- -free and sulphidic samples differed only in their total-S values significantly, with higher total-S contents in NO_3^- -free samples.

5 Therefore, we discussed the partial data-sets of NO_3^- -free and NO_3^- -bearing samples only when significant differences to subgroups according to sediment properties occurred.

3.2 Time course of denitrification products, denitrification rates and denitrification capacity

10 The denitrification rates of non-sulphidic and NO_3^- -bearing samples were significantly lower than those of sulphidic and NO_3^- -free samples (kw: $P < 0.01$) (Table 2 and Fig. 1). Almost all of the transition zone samples exhibited a clear flattening of the slopes of denitrification derived ($\text{N}_2 + \text{N}_2\text{O}$) concentration curves, i.e. showed decreasing denitrification rates over time (Fig. 1b). Non-sulphidic samples showed a relative constant 15 production of ($\text{N}_2 + \text{N}_2\text{O}$) (Fig. 1a), but long-term denitrification rates were highly significant (kw: $P < 0.001$) lower compared to sulphidic samples (Table 2, Fig. 1).

Both FFA and GKA aquifer material had nearly the same median initial denitrification rates ($D_r(7)$) with values of 33.8 and $31.2 \mu\text{g N kg}^{-1} \text{d}^{-1}$, respectively, whereas the maximal $D_r(7)$ of GKA material was over 50 % higher compared to the FFA material (Table 2). At the end of incubation, samples from the FFA and GKA had a comparable range of denitrification capacities (D_{cap}) (up to $56 \text{ mg N kg}^{-1} \text{yr}^{-1}$). Sulphidic samples had significantly higher median $D_r(7)$ and D_{cap} ($35.6 \mu\text{g N kg}^{-1} \text{d}^{-1}$ and $15.6 \text{ mg N kg}^{-1} \text{yr}^{-1}$, respectively) than non-sulphidic samples ($11.5 \mu\text{g N kg}^{-1} \text{d}^{-1}$ and $1.6 \text{ mg N kg}^{-1} \text{yr}^{-1}$, respectively) (kw: $P < 0.001$) (Table 2). Non-sulphidic samples exhibited higher initial denitrification rates ($D_r(7)$) than long-term denitrification rates ($D_r(365)$), whereas this was vice versa for sulphidic samples. Transition zone samples were similar in $D_r(7)$ compared to sulphidic material, but D_{cap} was about 25 % lower.

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After the intensive treatment incubated aquifer samples were 1 to 17 times higher in $D_r(7)$ and between 4 to 17 times higher in D_{cap} compared to the standard treatment (Table S2 in the Supplement). But the intensive treatment did not lead to a complete exhaustion of the stock of reactive compounds during incubations, i.e. samples still exhibited denitrification rates at the end (Fig. 1d).

3.3 Sediment parameters

C_{org} exhibited large ranges of similar magnitude in both aquifers (203–5946 and 76–8972 mg C kg⁻¹ in the FFA and GKA aquifer samples, respectively) (Table 1). The same applied for total-S, (29–603 and 36–989 mg S kg⁻¹) and $SO_4^{2-}_{extr}$ (0.9 to 25 and from 10 0.3 to 20 mg S kg⁻¹). GKA samples contained significantly lower median DOC_{extr} values than FFA material (9.2 and 6.1 mg C kg⁻¹, respectively). $SO_4^{2-}_{extr}$ and DOC_{extr} decreased with depth in the FFA (r_s : $R = -0.83$ and $R = -0.86$, respectively, $P < 0.001$) and in the GKA (r_s : $R = -0.54$ and $R = -0.59$, respectively, $P < 0.05$). The ranges of C_{hws} were comparable for FFA and GKA material (Table 1). C_l values of FFA and GKA 15 samples were statistical not different from each other, but maximum values in GKA samples were almost 3 times higher than in FFA material (Table 1). Overall, 19 % and 29 % of the C_{org} in the GKA and FFA aquifer material, respectively, belonged to the fraction of C_l . Statistical significant differences (kw: $P < 0.05$) occurred between the groups of non-sulphidic and sulphidic aquifer material with a ratio of C_l to C_{org} by 0.16 and 0.24, respectively. Similar differences and ratios applied for the groups of NO_3^- -bearing and NO_3^- -free samples (Table 1). Except for values of total-S and DOC_{extr} , the investigated sediment parameters exhibited no significant differences between FFA and GKA aquifer material (Fig. S1 in the Supplement). All sediment variables showed significant differences (kw: $P < 0.05$) between the 3 groups of non-sulphidic, sulphidic 20 and transition zone samples (Fig. S1 in the Supplement). On average, transition zone samples had lower ranges in all sediment parameters than sulphidic material except in C_{hws} and DOC_{extr} . Non-sulphidic samples exhibited lower average concentrations 25

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in the independent sediment variables compared to transition zone samples, except for $\text{SO}_4^{2-}_{\text{extr}}$ and DOC_{extr} for which the opposite was the case (Table 1, Fig. S1 in the Supplement).

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3.4 The stock of reactive compounds and its availability for denitrification during incubation

3.4.1 Standard treatment

The stock of reduced compounds (SRC) of FFA and GKA aquifer material differed not significantly from each other (0.22–5.9 and 0.97–8.9 g N kg^{-1} , respectively) (Table 2 and Fig. 2a). In contrast, the median SRC of sulphidic aquifer material (1.3 g N kg^{-1})

10 was 2 and 5 times higher compared to the non-sulphidic (0.24 g N kg^{-1}) and transition zone material (0.67 g N kg^{-1}). The fraction of SRC available for denitrification during incubation (αF_{SRC}) in the FFA material ranged from 0.08 to 5.44 % and was significantly higher than the range of αF_{SRC} of GKA material (0.36 to 1.74 % αF_{SRC}) (Fig. 2b). Transition zone samples exhibited the highest median αF_{SRC} values (1.65 %), followed by sulphidic (1.16 %) and non-sulphidic aquifer material with the lowest αF_{SRC} values (0.47 %). Statistical significant differences were only found between non-sulphidic samples and the previous two groups (Fig. 2b).

15

3.4.2 Intensive treatment

20 Since we used parallel samples for the intensive and standard treatments, the SRC was identical for both treatments. Also the intensive treatment was not able to exhaust the denitrification capacity of the incubated aquifer material during incubation (Fig. 1). The αF_{SRC} derived from intensive incubations was 3.7 to 17 times higher compared to the standard treatment (Table S2 in the Supplement, αF_{SRC} values of the intensive treatment are given in parentheses).

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3.5 Relationship between denitrification capacity and sediment parameters

Correlations between D_{cap} and sediment parameters showed substantial differences among the various partial data-sets (Table 3). For the full data-set C_{org} exhibited the closest correlation ($r_s: R = 0.72, P < 0.001$) with D_{cap} . In the FFA aquifer material, 5 DOC_{extr} and $SO_4^{2-}_{extr}$ showed highly significant negative relations to D_{cap} (Table 3). The relation between these parameters and D_{cap} was only poor or not significant for the rest of sub data-sets. C_{hws} exhibited the highest positive correlations with D_{cap} in the partial data-sets with samples containing relatively low concentrations of sulphides (Table 1), i.e. the data-sets of non-sulphidic and transition zone samples ($r_s: R = 0.85$ 10 and $R = 0.60$, respectively, $P < 0.001$). C_I was in closest relation with D_{cap} in GKA and non-sulphidic samples ($r_s: R = 0.87$ and $R = 0.73$, respectively, $P < 0.01$). C_{hws} and C_I were more closely related to D_{cap} compared to C_{org} within sub-groups of aquifer material with no or only low contents of total-S (data not shown). In contrast to GKA, the 15 FFA aquifer material exhibited good correlations between C_{hws} and D_{cap} ($r_s: R = 0.58, P < 0.01$) (Table 3). In all data-sets, the silt content was significantly positively correlated with D_{cap} , except for transition zone aquifer material where this relation was not significant. For the full data-set and FFA and GKA data-sets, total contents of C_{org} and sulphur were in closest positive correlation with D_{cap} . In the partial data-sets which were 20 differentiated according to chemical parameters, these relations were less pronounced or not significant.

3.6 Regression models to predict long-term denitrification (D_{cap})

3.6.1 Predicting D_{cap} from initial denitrification rates

Initial denitrification rates derived after 7 days of incubation ($D_r(7)$) exhibited only good linear relations with D_{cap} for non-sulphidic samples (with sub-sets of FFA and GKA non-sulphidic samples) and for the group NO_3^- -bearing samples with correlation coefficients 25 >0.86 (Table 4). For the other data-sets, D_{cap} was not predictable by $D_r(7)$ (Table 4 and

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Fig. 3). Moreover, especially sulphidic and NO_3^- -free samples, exhibited a considerable lag-phase at the beginning of incubation, which resulted in poor predictions of D_{cap} from $D_r(7)$. In contrast to $D_r(7)$, the average denitrification rate after 84 days of incubation, i.e. at the next sampling time $D_r(84)$, showed good to excellent regressions ($R > 0.78$) with D_{cap} for the full and most of the partial data-sets. An exception were the transition zones samples which showed declining denitrification rates during incubation.

3.6.2 Predicting D_{cap} from sediment parameters

Simple regression and multiple regression analysis was performed to predict D_{cap} from independent sediment variables, i.e. the silt content, C_{org} , total-S, SO_4^{2-} extr, DOC_{extr} , C_{hws} and C_{l} . The goodness of fit between modelled and measured D_{cap} is given by correlation coefficients, the ratio of calculated to measured D_{cap} ($R_{\text{c/m}}$) and the average deviation of $R_{\text{c/m}}$ from the mean in the various sub data-sets.

Simple regression models yielded a significant lower goodness of fit than multiple regressions (Table 5, Tables S3 and S4 in the Supplement). Simple regressions with individual sediment parameters demonstrated that C_{org} and C_{l} yielded best predictions of D_{cap} when the whole data-set was analysed (Table S3 in the Supplement). Regression analysis of partial data-sets grouped according to chemical properties, i.e. groups including samples from both aquifers, resulted in R values below 0.8 for all tested variables. For the sulphidic samples, C_{org} or C_{l} values were the best individual sediment parameters to model D_{cap} when considering partial data-sets including samples from both aquifers. For the individual aquifers, some single sediment parameters were very good estimators ($R > 0.8$) for D_{cap} , e.g. total-S and DOC_{extr} in the FFA data-set and C_{org} , total-S and C_{l} for GKA. C_{org} was clearly less correlated with D_{cap} in those sub-groups of aquifer material with low contents of SRC, i.e. the non-sulphidic aquifer material.

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Combinations of total-S and C_{org} did not substantially increase the goodness of fit of the regression models to predict D_{cap} in comparison to simple regressions with these two variables (Table 5, selection I in comparison to Table S3 and S4 in the Supplement), in some cases the goodness of fit even worsened. Only for the partial data-sets of non-sulphidic samples a linear combination of these two variables was slightly better than a simple regression with one of the independent variables.

Table 5, selection II lists the combinations including C_{org} , total-S, C_l , and $SO_4^{2-}^{extr}$ which revealed the highest correlation coefficient with D_{cap} for the corresponding data-sets. Compared to simple regressions these linear combinations improved correlation coefficients of regressions for most partial data-sets. Also the range of deviations of calculated from measured D_{cap} values ($R_{c/m}$) was smaller (Table S4 in the Supplement). For the full data-set and the sulphidic samples for example, the correlation coefficient R increased from 0.80 to 0.86 and from 0.66 to 0.79, respectively, if instead of regressions between C_{org} and D_{cap} the combination of C_{org} - C_l was used to model D_{cap} . This combination was also better than regressions with C_l alone (Table 5 in comparison to Table S4 in the Supplement). The combination of total-S and $SO_4^{2-}^{extr}$ improved the correlation coefficient with D_{cap} in comparison to simple regression with total-S clearly for all sub data-sets containing sulphidic aquifer material. For FFA samples this combination raised R of the simple regressions from 0.83 to 0.89.

For all data-sets, except the sub dataset of sulphidic material, multiple regressions between D_{cap} and all 7 independent sediment parameters (direct multiple regression) yielded correlation coefficients $R > 0.92$ (data not shown), i.e. over 84 % of the variance of the measured D_{cap} values could be explained with this regression. For sulphidic aquifer material, R was 0.83. A stepwise multiple regression, which gradually adds the sediment parameters to the regression model according to their significance yielded results which were almost identical to the results of direct multiple regression (Table 5, selection III). The stepwise multiple regression model reduced the number of needed regression coefficients (i.e. the number of needed sediment variables) to model D_{cap} from 7 to 3 or 5. The goodness of fit as indicated by mean $R_{c/m}$ values close to 1 and

small ranges of $R_{c/m}$ values was usually the best with multiple regression analysis, especially for samples with D_{cap} values below $20 \text{ mg N kg}^{-1} \text{ yr}^{-1}$ (Table S4 in the Supplement).

3.7 Minimal lifetime of denitrification (emLoD)

5 The minimal lifetime of denitrification (emLoD) of the incubated aquifer material was estimated for a nitrate input of $11.3 \text{ g NO}_3^- \text{-Nm}^{-2} \text{ yr}^{-1}$ as described in Sect. 2.5. With this nitrate input and an aF_{SRC} of 5 % the calculated emLoD of one m^3 of aquifer material ranged between 0.7–8 and $2.4\text{--}67 \text{ yr m}^{-1}$ for non-sulphidic and sulphidic aquifer material, respectively (Tables 2 and S2 in the Supplement). The estimated median em-
10 LoD of sulphidic material was 5 times higher then the one of non-sulphidic samples. FFA and GKA samples differed statistical not significantly in their emLoD values ($kw: P < 0.05$) (median emLoD values of NO_3^- -free aquifer samples from the FFA and GKA are $19.8 \pm 15 \text{ yr}$ and $10.5 \pm 20 \text{ yr}$, respectively; see also Table S2 in the Supplement).

4 Discussion

15 4.1 Groundwater redox state and sample origin

The non-sulphidic aquifer material in this study, which exhibited low denitrification rates, originated generally from aquifer regions with dissolved O_2 concentrations $>1.5 \text{ mg l}^{-1}$ ($= 42 \mu\text{mol O}_2 \text{ l}^{-1}$) and is already largely oxidized. This aquifer parts could be referred to as aerobic ($1\text{--}2 \text{ mg O}_2 \text{ l}^{-1}$, Rivett et al., 2008). In laboratory experiments with ho-
20 mogeneous material the intrinsic O_2 threshold for the onset of denitrification is between 0 and $10 \mu\text{mol O}_2 \text{ l}^{-1}$ (Seitzinger et al., 2006). Reported apparent O_2 thresholds for denitrification in aquifers are between 40 to $60 \mu\text{mol l}^{-1}$ (Green et al., 2008, 2010; McMahon et al., 2004; Tesoriero and Puckett, 2011). Green et al. (2010) modelled the apparent O_2 threshold for denitrification in a heterogeneous aquifer and found that an

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apparent O_2 threshold obtained from groundwater sample analysis of $<40\text{ O}_2\text{ }\mu\text{mol l}^{-1}$ is consistent with an intrinsic O_2 threshold of $<10\text{ }\mu\text{mol l}^{-1}$. This apparent threshold of $40\text{ }\mu\text{mol O}_2\text{ l}^{-1}$ corresponds well with the threshold of minimal and maximal dissolved O_2 concentrations at the origins of non-sulphidic and sulphidic aquifer material, respectively, in both aquifers.

4.2 Predicting D_{cap} from initial denitrification rates and time course of denitrification

The ultimate goal of our research program is to predict long-term denitrification capacity (D_{cap}) from initial denitrification rates. This is to facilitate determination of D_{cap} since laboratory measurements of initial denitrification rates ($D_r(7)$) are more rapid and less laborious and expensive compared to long-term incubations to measure D_{cap} . Moreover, initial denitrification rates can also be measured in situ at groundwater monitoring wells (Konrad, 2007; Well et al., 2003) and can thus be determined without expensive drilling for aquifer material. Konrad (2007) tested this approach with a small data set (13 in situ measurements) and 26 pairs for $D_r(7)$ vs $D_r(\text{in situ})$ and only 5 pairs for $D_r(\text{in situ})$ vs. D_{cap} . One objective of this study is to develop transfer functions to predict D_{cap} from $D_r(7)$. The next step is to compare in situ denitrification rates ($D_r(\text{in situ})$) from push-pull experiments at the location of the incubated aquifer samples with their D_{cap} measured in this study and to check how precise D_{cap} can be derived from $D_r(\text{in situ})$.

By and large, our measurements of D_{cap} agreed well with previous long-term laboratory incubation studies with sediments from Pleistocene sandy aquifers. Well et al. (2005) and Konrad (2007) report total ranges for D_{cap} of 9.5 to $133.6\text{ mg N kg}^{-1}\text{ yr}^{-1}$ and 0.99 to $288.1\text{ mg N kg}^{-1}\text{ yr}^{-1}$, respectively. Weymann et al. (2010) conducted incubations with aquifer material from one location within the FFA, reporting ranges of D_{cap} of heterotrophic (\approx non-sulphidic) and autotrophic (\approx sulphidic) aquifer material between $1\text{--}12.8$ and $14.5\text{--}103.5\text{ mg N kg}^{-1}\text{ yr}^{-1}$, respectively. All of these denitrification capacities are comparable to our findings (Table 2),

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indicating that the selection of our sites and sampling location represent the typical range of denitrification properties of this kind of Pleistocene sandy aquifers.

Two aspects have to be considered when using $D_r(7)$ as an indicator for D_{cap} : (i) the availability of reactive compounds may change during incubation and (ii) different microbial communities resulting from the availability of different electron donors and acceptors may be evident in samples from different aquifer redox zones (Griebler and Lueders, 2009; Kölbelboelke et al., 1988; Santoro et al., 2006) and possible shifts within the microbial community during incubation have thus to be taken into account (Law et al., 2010).

With respect to (i), it is straightforward that the availability of reduced compounds for denitrification in aquifer material directly influences the measured denitrification rates since denitrification is a microbially mediated process and the significant majority of microbes in aquifers are attached to surfaces and thin biofilms (Griebler and Lueders, 2009; Kölbelboelke et al., 1988). Therefore, the area of reactive surfaces of reduced compounds within the sediment might control the amount of active denitrifiers in an incubated sample and thus the measured denitrification rates and vice versa. Therefore, denitrification rates are an indirect measure of the availability of reduced compounds for denitrification and the availability of reduced compounds may reduce due to oxidation during incubation. On the contrary, growth of the microbial community may change the apparent availability of reduced compounds due to the increase of the area of “colonised” reduced compounds within the incubated aquifer material and thus leading to increasing denitrification rates during incubation.

The almost linear time-course of denitrification in non-sulphidic and sulphidic samples (Fig. 1a, c) indicate minor changes of the availability of reduced compounds during incubation. The linear-time-courses also suggest a pseudo-zero-order kinetic of denitrification where denitrification rates are independent from changes of NO_3^- or reduced compounds during the incubations. NO_3^- concentrations in the batch solution of incubated samples were always above 3.0 mg NO_3^- -N during the whole incubation period

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and thus above the reported threshold of $1.0 \text{ mg NO}_3^- \text{-NI}^{-1}$, below which denitrification becomes NO_3^- limited (Korom et al., 2005; Morris et al., 1988; Wall et al., 2005).

The small denitrification rates measured in the non-sulphidic samples may then be the result of only small amounts of organic carbon oxidized during denitrification. The consumed fraction of available organic carbon might release fresh surfaces which can further be oxidized during denitrification. The relative stable denitrification rates of non-sulphidic samples may then reflect that the area of microbial available surface of reduced compounds exhibits negligible change during incubation. This is plausible for the case that the surface of the organic matter is relatively small in comparison to its volume, which applies to the lignitic pebbles in the FFA (Frind et al., 1990).

Most of the sulphidic aquifer samples from the zone of NO_3^- -free groundwater in both aquifers showed also relative constant linear increase of denitrification products during incubation (Fig. 1c). This aquifer material was not yet in contact with dissolved O_2 and NO_3^- from the groundwater. Hence, the reduced compounds, if initially present in the solid phase, are supposed to be not yet substantially depleted. The relative constant linear increase of denitrification products of these samples suggests that the denitrifying community had a relative constant activity during incubation, implying a constant amount of denitrifying microbes and thus constant areas of reactive surfaces. In contrast, almost all transition zone samples exhibited clearly declining denitrification rates during incubation (Fig. 1b). This group represents aquifer material already depleted in reduced compounds (Table 1 and Fig. 2a) but still containing residual contents of reactive sulphides and therefore showing an $\text{SFC} > 1 \text{ mg SO}_4^{2-} \text{-Skg}^{-1} \text{ yr}^{-1}$. These residual sulphides might be relatively fast exhausted during incubation leading to a loss of reactive surfaces and in the following to a flattening of the slope of measured denitrification products ($\text{N}_2 + \text{N}_2\text{O}$).

The intensive incubation experiment gave up to 17 times higher denitrification rates than the standard incubations (Table S2 in the Supplement) and differed from the standard incubations only in three points: (i) dilution of aquifer material with pure quartz sand, (ii) higher incubation temperatures (20°C instead of 10°C) and (iii) continuous

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shaking of the incubated sediments on a rotary shaker. The denitrification activity of the added pure quartz was found to be negligible. Well et al. (2003) evaluated the temperature effect on denitrification rates measured during laboratory incubations. An increase of incubation temperature from 9 to 25 °C resulted in 1.4 to 3.8 times higher denitrification rates. In contrast to this the intensive incubation experiment presented in this study gave up to 17 times higher denitrification rates than the standard incubations. This suggests that not only higher temperatures but also the continuous shaking of the incubated aquifer material may have led to higher denitrification rates by the enlargement of the surfaces of reduced compounds within the aquifer material due to physical disruption of pyrite and/or organic carbon particles. The latter was visible as black colouring of the batch solution which was not noticeable at the beginning of intensive incubations and also not during the standard incubations. But in contrast to our expectations, the intensive treatment did not lead to a faster decline of denitrification rates during incubation (Fig. 1d). The reasons for this might be that the loss of reactive surfaces of reduced compounds due to consumption during denitrification was small compared to their amount. Also the shaking might have contributed to the creation of reactive surfaces and thus may have supported denitrification. A possible temperature effect on the suit of active denitrifiers during incubations and from this on the resulting denitrification rates was not investigated during this study, but should be considered in further studies.

With respect to the importance of changes in the availability of electron acceptors for the communities of active microbes present in aquifer material (aspect ii), we assume that in the sulphidic samples from the zone of NO_3^- -free groundwater, the population of denitrifiers had to adapt to the addition of NO_3^- as a new available electron donor, e.g. by growth of denitrifying population and changes in the composition of the microbial community (Law et al., 2010). This adaptation processes require time and might be a reason for the missing correlation between $D_r(7)$ and D_{cap} during incubation of sulphidic samples in both aquifers, whereas $D_r(84)$ was a good predictor for D_{cap} (Fig. 3 and Table 4). This explanation is in line with the fact that spatial heterogeneity

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4.3 Predicting D_{cap} of aquifer sediments, correlation analysis and regression models

4.3.1 Sediment parameters and their relation to D_{cap}

Correlation analysis

5 C_{org} , $SO_4^{2-}_{extr}$, C_{hws} and C_l exhibited no significant differences between both aquifers, whereas the amount of total-S was significantly higher and DOC_{extr} values significantly lower for GKA compared to FFA samples. But in contrast, the opposite groups of non-sulphidic to sulphidic aquifer material differed significantly in all of the analysed independent sediment variables (kw: $P < 0.05$) (Table 1 and Fig. S1 in the Supplement).

10 The same applies also for the opposite groups of NO_3^- -free and NO_3^- -bearing aquifer material (data not shown).

The measured range of DOC_{extr} (4.7 to 11.6 mg C kg $^{-1}$) for FFA and GKA aquifer samples are in the range of recently reported values (Weymann et al., 2010) for aquifer samples from the same site at comparable depths. The DOC_{extr} values clearly decreased with depth in both aquifers (Table S1 in the Supplement) and exhibited significant negative correlations with the D_{cap} of the incubated aquifer material (Table 3) (r_s : $P < 0.05$). Similarly, von der Heide et al. (2010) reported significant negative correlation between DOC and the concentrations of N_2O as an intermediate during reduction of NO_3^- to N_2 in the upper part of the FFA. From these findings we suppose that the reactive fraction of DOC is increasingly decomposed or immobilized with depth in both aquifers. Moreover, the negative correlation between the DOC_{extr} and the measured D_{cap} suggests that the contribution of DOC_{extr} to denitrification capacity of the aquifers is relatively small, which is consistent with findings of (Tesoriero and Puckett, 2011) and (Green et al., 2008).

25 The highest concentrations of $SO_4^{2-}_{extr}$ were measured in samples from the upper parts of both aquifers (Table 1). The measured range of $SO_4^{2-}_{extr}$ (Table 1) exhibited significant negative correlations between D_{cap} of FFA and GKA aquifer material (r_s :

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$R = -0.82$ and $R = -0.49$, respectively, $P < 0.05$) (Table 3). $\text{SO}_4^{2-}_{\text{extr}}$ values decreased with depths in both aquifers (Table S1 in the Supplement) and thus exhibited an inverse concentration gradient compared with total-S values. The range of $\text{SO}_4^{2-}_{\text{extr}}$ of FFA and GKA material is comparable to $\text{SO}_4^{2-}_{\text{extr}}$ values ($20.5 \pm 16.7 \text{ mg SO}_4^{2-}\text{-S kg}^{-1}$) of aquifer samples from North Bavaria, from a deeply weathered granite with a sandy to loamy texture (Manderscheid et al., 2000). All measured $\text{SO}_4^{2-}_{\text{extr}}$ values above 10 mg Skg^{-1} from FFA and GKA samples (except for the samples from 25.9–26.9 m and 27–28.3 m below surface in the GKA) originated from zones within these two aquifers with pH values of the groundwater between 4.39 and 5.6 (von der Heide unpublished data and own measurements). According to the pH values, the groundwater from these locations is in the buffer zone of aluminium hydroxide and aluminium hydroxysulfates (Hansen, 2005). It is known that hydroxysulphate minerals can store SO_4^{2-} together with aluminium (Al) in acidic soils (Khanna et al., 1987; Nordstrom, 1982; Ulrich, 1986) and aquifers (Hansen, 2005). Therefore, dissolution of aluminium hydroxysulphate minerals may have lead to the higher values of $\text{SO}_4^{2-}_{\text{extr}}$ in samples from the upper already oxidized parts of both aquifers.

KMnO_4 labile organic carbon (C_l) measured in the aquifer material was closely related to C_{org} ($r_s: R = 0.84, P < 0.001$). GKA samples showed a much wider range of values (0.9 to $2504.7 \text{ mg C kg}^{-1}$) than FFA aquifer material (2.7 to 887 mg C kg^{-1}) (Table 1). The total average of C_l/C_{org} ratios of 0.24 for the full data-set is comparable to the mean ratio of 0.3 reported by Konrad (2007) for 3 comparable sandy aquifers, showing that typically less than half of C_{org} in Pleistocene aquifers is KMnO_4 labile. The higher C_l/C_{org} ratio in the sulphidic samples might indicate that the C_l fraction of C_{org} in the upper non-sulphidic parts of both aquifers is already oxidized to a larger extent (Table 1). Konrad (2007) assumes that C_l represents the proportion of C_{org} which might be available for microbial denitrification. A stoichiometric $\text{CH}_2\text{O}_{(\text{Corg})}/\text{NO}_3^-$ -N ratio of 1.25 (Korom, 1991) leads to the conclusion that the amount of C_l was always higher than the measured denitrification capacity (D_{cap}) of the several aquifer samples.

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This shows that a significant fraction of C_i did not support a fast denitrification. It can thus be assumed that C_i represents rather an upper limit for the bioavailable organic carbon in the incubated sediments. However, among the sediment parameters C_i was the best predictor of D_{cap} for GKA samples and non-sulphidic aquifer material and also a comparatively good predictor with respect to the full data-set (Table 3).

The values of hot water extracts (C_{hws}) from FFA and GKA aquifer material with the ranges of 0.01–42.6 and 14.9–58.5 mg C kg⁻¹, respectively, are comparable to the range of C_{hws} of 6.2 to 141 mg C kg⁻¹ given by Konrad (2007). C_{hws} represents on average a proportion of 6.5 % of the entire C_{org} pool in the aquifer material from FFA and GKA. This value is similar to the proportion of 5 % C_{hws} of the entire C_{org} reported by Konrad (2007), with significantly (kw: $P < 0.05$) higher percentages in the non-sulphidic (12.5 %) compared to the sulphidic samples (3.7 %). We found high to very high and highly significant correlations between C_{hws} and D_{cap} of non-sulphidic material (Table 3) and NO_3^- -bearing samples (r_s : $R = 0.85$ and $R = 0.74$, respectively, $P < 0.001$). Studies on C_{hws} stability in soil organic matter revealed that C_{hws} is not completely bioavailable (Chodak et al., 2003; Sparling et al., 1998). Moreover, these authors conclude that C_{hws} is not a better measure of the available soil organic carbon than total C_{org} values. Balesdent (1996) concluded from natural ¹³C labelling technique (long-term field experiments with maize) that coldwater extracts contain amounts of slowly mineralizable “old” C_{org} pools and this can also be expected for hot water extracts. The close correlation between C_{hws} and D_{cap} in the non-sulphidic aquifer material and not for deeper sulphidic aquifer material is distinctive and suggests that bioavailable fraction of C_{hws} in the upper part of both aquifers might be higher compared with deeper aquifer regions.

The measured C_{org} values of FFA and GKA aquifer material (Table 1) are comparable to ranges reported by Konrad (2007), Strelbel et al. (1992) and Hartog et al. (2004) (Pleistocene fluvial and fluvio-glacial sandy aquifers in Northern Germany and the eastern part of The Netherlands). The total sulphur contents of FFA and GKA aquifer samples are also comparable to the ranges reported by these authors, except Hartog et al. (2004) who reported 4 to 5 times higher total-S contents. Bergmann (1999) and Konrad

(2007) investigated the distribution of S species in aquifer material from sandy aquifers in North Rhine-Westphalia and Lower Saxony, Germany, respectively, and found that 80 to over 95 % of the total-S value is represented by sulphide-S.

4.3.2 Predicting D_{cap} from sediment variables

5 Single sediment parameters like C_{org} , C_l or total-S are partly good to very good estimators for the measured D_{cap} in our data-set (Table S3 in the Supplement). Grouping of aquifer material according to hydro-geochemical zones strongly increases the predictive power of single independent sediment parameters with respect to the measured denitrification capacity (Tables 4 and S3 in the Supplement). For example, C_{org} and C_l values are very good parameters to predict D_{cap} for GKA aquifer material, which 10 almost linearly increased with measured C_{org} and C_l values. The predictability of D_{cap} with simple regressions, linear combinations of two sediment parameters and multiple regressions was best when these models were applied to partial data-sets of one aquifer, whereas predictions were always worse when samples from both aquifers were 15 included (Tables 5 and S3 in the Supplement). For example, total-S values exhibited good simple regressions ($R > 0.8$) with partial data-sets that contain only aquifer material from one aquifer. Conversely, the linear correlation coefficients between total-S and D_{cap} of sulphidic aquifer material and NO_3^- -free samples (both groups contain FFA and GKA aquifer material) were relatively low with R of 0.4 and 0.32, respectively. The proportion 20 of total-S in SRC of the GKA samples was 3 times higher than in samples from the FFA, whereas the share of sulphides contributing to the measured denitrification capacity was almost the same in FFA and GKA material during incubation (Fig. 2b). This shows that samples from both sites were distinct in the reactivity of sulphides which may be related to the geological properties of the material including the mineralogy 25 of the sulphides and the origin of the organic matter.

C_{org} and total-S can be seen as integral parameters with no primary information about the fraction of reactive and non-reactive compounds (with regard to denitrification) represented by these parameters. As already discussed above, C_l might be an

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upper limit for the fraction of microbial degradable organic carbon as part of total organic carbon (C_{org}) in a sample of aquifer material. In our data-set, C_1 exhibited better regressions with D_{cap} than C_{org} for aquifer material with relatively low D_{cap} , i.e. non-sulphidic aquifer material and transition zone samples (Table S3 in the Supplement). In

5 these two partial data-sets it can be assumed that the reduced compounds available for denitrification are already depleted by oxidation with NO_3^- and dissolved O_2 . The median C_{org} contents of non-sulphidic and transition zone samples were below 60 % of the one of NO_3^- -free samples (Table 1). Hence, C_{org} in non-sulphidic and transition zone samples represents less reactive residual C_{org} compared to aquifer material which was

10 not yet in contact with groundwater NO_3^- or dissolved O_2 . This might be the reason for the comparatively low correlation of C_{org} and D_{cap} in the depleted aquifer material of non-sulphidic and transition zone samples. Similar to this finding, Well et al. (2005) reported poor correlations between C_{org} and D_{cap} for hydromorphic soil material with low measured D_{cap} during incubation.

15 Multiple regression analysis clearly enabled the best prediction of D_{cap} . Except for sulphidic samples, correlation coefficients >0.91 were achieved for all other partial data-sets (Table 5). But multiple regression models are of limited practical use because the measurement of several sediment parameters is time consuming and expensive.

The goodness of fit of the regression models was highly variable. Simple regressions, 20 linear combinations of two sediment variables and multiple regression analysis could predict the order of magnitude of D_{cap} . The uncertainty of calculated D_{cap} as given by the ratio of calculated D_{cap} vs. measured D_{cap} ($R_{c/m}$) was within a range of 0.5 to 2 for aquifer material with a measured $D_{cap} > 20 \text{ mg N kg}^{-1} \text{ yr}^{-1}$ when simple regressions models with C_{org} and total-S and multiple regressions were applied (Table S4 in the 25 Supplement). In case of less reactive aquifer material ($D_{cap} < 20 \text{ mg N kg}^{-1} \text{ yr}^{-1}$), only multiple regressions were able to predict D_{cap} within this range of uncertainty, whereas simple regressions models yielded poor fits. Well et al. (2005) performed long-time anaerobic incubations with soil material of the saturated zone of hydromorphic soils

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from Northern Germany in order to measure and calculate D_{cap} . They used multiple regression models to model D_{cap} from independent sediment variables. Similar to our finding, they report that prediction of D_{cap} with regression models was unsatisfactory for samples with low measured denitrification capacity ($D_{cap} < 36.5 \text{ mg N kg}^{-1} \text{ yr}^{-1}$, this threshold fits also to our data) and they presumed that a considerable variability in the fraction of reactive organic carbon in the measured C_{org} is the reason for this observation.

4.4 Assessment of the lifetime of denitrification within the investigated aquifers

The data-set provides spatial distribution of D_{cap} and SRC values in both aquifers, allowing the estimation of lifetime of denitrification with Eq. 2 as well as the estimation of the depth shift of the denitrification front in both aquifers. To calculate the emLoD of aquifer samples an average fraction of SRC available for denitrification (aF_{SRC}) of 5 % was assumed. This value was assumed from intensive incubation with median aF_{SRC} of 6.4 % and the fact that denitrification did not stop during all incubations (Fig. 1) and thus the real aF_{SRC} of the incubated aquifer samples were higher than the measured ones (Table S2 in the Supplement).

The simplified approach of calculating emLoD with Eq. 2 implicitly assumes that the residence time of groundwater in 1 m^3 aquifer material is sufficient to denitrify the nitrate input coming with groundwater recharge, if the amount of microbial available SRC is big enough to denitrify the nitrate input. If the residence time is to short, NO_3^- would reach the subsequent m^3 of aquifer material with groundwater flow, even if the first m^3 still posses an SRC available for denitrification. This means the denitrification front would have a thickness of more than 1 m and the real lifetime of denitrification within one m^3 would be longer then predicted by Eq. 2. This was the case at multilevel wells B2 and N10 in the FFA in the depths between 8–10 and 4.5–8.6 m, respectively. At this depths the groundwater still contains NO_3^- , although the D_{cap} of the aquifer material was higher than the nitrate input ($6.6 \text{ mg N kg}^{-1} \text{ yr}^{-1}$). Two reasons might explain this,

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With respect to future groundwater quality, our estimates of emLoD show that denitrification capacity is exhaustible, but will last for several generations in both aquifers, if the NO_3^- -free anoxic groundwater zone extends over several meters of depth.

4.5 Are laboratory incubation studies suitable for the *in situ* process?

5 In the following a few conclusions from the presented study are given, trying to contribute to this question. Therefore, a couple of sub-problems arising from this question are discussed in the following.

4.5.1 Are the NO_3^- concentrations during incubation comparable to those *in situ* and what is their influence on the measured denitrification rates?

10 The NO_3^- concentrations in the FFA range from 0–43 (median 8.5) mg NI^{-1} and in the GKA from 0–57.6 (median 7.2) mg NI^{-1} (Well et al., 2012). The nitrate concentrations at the beginning of the batch experiments were in the range of 35 to 43 mg NI^{-1} , depending on the amount of pore water in the incubated sediments diluting the added tracer solution. During the incubation experiments the measured NO_3^- concentrations
15 were always between the ranges of NO_3^- concentrations found in both aquifers.

The almost linear time course of denitrification products (see Sect. 4.2) accompanied by a parallel decrease of NO_3^- concentrations in the batch solutions suggests that the

NO_3^- concentrations were of no or only minor importance for the measured denitrification rates during the conducted incubation experiments, i.e. the kinetics of denitrification

20 were zero-order. The presented experimental results are in accordance to several workers who reported that the kinetics of denitrification at NO_3^- concentrations above 1 mg NI^{-1} are zero-order, i.e. independent of the nitrate concentration, which suggest that the supply of electron donors controls the denitrification rates (Rivett et al., 2008).

In a recent publication Korom et al. (2012) stated that denitrification in aquifers appears to be most often reported as zero-order. This statement was based on Green et al. (2008) and Korom (1992) and citations therein. Similarly, Tesoriero and Puckett

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(2011) found that in most suboxic zones of 12 shallow aquifers across the USA in situ denitrification rates could be described with zero-order rates.

In accordance to the cited studies, the experimental results indicate that the supply of electron donors controlled the measured denitrification rates during the conducted 5 incubation experiments, rather than NO_3^- concentrations. Presumably this can also be expected in situ in both aquifers, if the observation period of rate measurements is short enough, so that the consumption of electron donors does not change the supply of denitrifiers with electron donors significantly. A decreasing concentrations of reduced 10 compounds supporting denitrification would lead to decreasing denitrification rates, i.e. to first-order rates. From this findings it might be concluded that the comparability of laboratory and in situ denitrification rates is less affected by the concentration of NO_3^- als long as denitrification becomes not NO_3^- limited, i.e. at NO_3^- concentrations 15 $>1 \text{ mg NI}^{-1}$.

4.5.2 Is one year incubation suitable to predict the denitrification capacity over many decades in an aquifer?

Our experiments are an approach to narrow down the real denitrification capacity of the investigated aquifer. Longer incubation periods would have been better, but there are always practical limits and incubation experiments could not be conducted over several decades.

20 The linear time course of denitrification during standard incubation of aquifer material from the NO_3^- -free zone of both aquifers and the considerably higher fraction of reductants available for denitrification during intensive incubation indicate that an estimation of at least a minimal denitrification capacity was possible from our experiments. During the intensive incubation experiment 4.6 to 26.4 % of the stock of reduced compounds 25 (SRC) of the incubated aquifer material was available for denitrification with median values of 6.4 % (Table S2 in the Supplement). From the results of standard and intensive incubations it was assumed that 5 % of the SRC is available for denitrification in

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the investigated sediments. The SRC of aquifer material from the zone of NO_3^- -bearing groundwater was only 40 % compared to the SRC present in aquifer material from the zone of NO_3^- -free groundwater in both aquifers (Table 2), suggesting that an availability of 5 % of the SRC did not over estimated the denitrification capacity of the investigated aquifers.

4.5.3 Did laboratory incubation studies really indicate what happens in situ?

They did not exactly retrace all processes contributing to the reduction of NO_3^- to N_2 and N_2O and their interaction under in situ conditions. But laboratory incubations might allow to get estimates of the amount of reduced compounds present in the incubated aquifer material that are able to support denitrification. And laboratory incubations should be compared with in situ measurements to check the meaningfulness of laboratory incubations for the in situ process. In a second study to follow we will compare laboratory incubations and in situ measurements at the origin of the incubated aquifer material.

5 Conclusions

We investigated the relationship between long-term denitrification capacity (D_{cap}), actual denitrification rates and different sediment parameters of aquifer samples during long-term anaerobic incubation experiments with sediment material from two Pleistocene unconsolidated rock aquifers. This was done to characterize exhaustion of denitrification capacity in the two aquifers and to further develop approaches to predict this process and D_{cap} .

Measured denitrification rates coincided with previous studies in comparable aquifers suggesting that the results derived in this study are transferable to other aquifers.

D_{cap} could be estimated from actual denitrification rates in samples that originated from regions within both aquifers that where already in contact with NO_3^- bearing

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kinetics, suggesting that denitrification was independent from the NO_3^- concentration during incubation of these samples. For the progressing exhaustion of reductants in denitrifying aquifers we suspect that the temporal dynamics is governed by the loss of reactive surfaces leading to reduced microbial habitats in the incubated sediment and to reduced denitrification rates, but this needs to be confirmed.

The protective lifetime of denitrification is limited in the investigated locations of the two aquifers but will last for several generations where the NO_3^- -free anoxic groundwater zone extends over several meters of depth. But where this zone is thin or contains only small amounts of microbial available reduced compounds it is needed to minimize anthropogenic NO_3^- input.

**Supplementary material related to this article is available online at:
[http://www.biogeosciences-discuss.net/9/8807/2012/
bgd-9-8807-2012-supplement.pdf](http://www.biogeosciences-discuss.net/9/8807/2012/bgd-9-8807-2012-supplement.pdf).**

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Table 1. Sediment parameters of the incubated aquifer material (medians with ranges in brackets).

Data-set	$\text{SO}_4^{2-\text{a}}$ mg Skg^{-1}	DOC^{b} mg Skg^{-1}	$\text{C}_{\text{hws}}^{\text{c}}$ mg Ckg^{-1}	C_l^{d} mg Ckg^{-1}	$\text{C}_{\text{org}}^{\text{e}}$ mg Ckg^{-1}	Total-S ^f mg Skg^{-1}	$\text{C}_l/\text{C}_{\text{org}}$
FFA	5.36 (0–25.2)	9.21 (5.7–11.6)	29.4 (0.01–42.6)	172.5 (2.7–887)	715.8 (203–5954)	72.3 (28.8–603)	0.165 (0.011–0.42)
GKA	10.52 (0.3–20.2)	6.11 (4.7–9.9)	29.1 (14.9–59)	239.8 (0.9–2505)	802.7 (75.9–8972)	509.6 (36.2–989)	0.264 (0.012–0.60)
non-sulphidic	14.46 (0.3–25.3)	8.96 (5.2–11.6)	21.6 (14.9–59)	91.2 (0.9–260)	236.7 (75.9–1047)	46.1 (28.8–196)	0.165 (0.011–0.42)
sulphidic	4.9 (0–20.2)	6.11 (4.7–10.8)	30.3 (0–42.6)	294.4 (39–2505)	1114.0 (232–8972)	463.7 (44.8–988.8)	0.239 (0.058–0.60)
transition zone	3.55 (0–12.8)	8.21 (6.2–10.8)	32.0 (22–42.5)	138.8 (82.2–463)	664.7 (311–1625)	53.2 (47.1–175.7)	0.226 (0.058–0.36)
NO_3^- -bearing	11.05 (0–25.3)	9.21 (6.2–11.6)	27.6 (14.9–44)	116.9 (0.9–463)	538.3 (75.9–1625)	49.3 (28.8–175.7)	0.191 (0.011–0.42)
NO_3^- -free	4.91 (0.3–20.2)	5.69 (4.7–9.9)	31.1 (20.8–59)	377.4 (37–2505)	1161.5 (232–8972)	510.4 (44.8–988.9)	0.267 (0.092–0.60)

^a Extractable sulfate-S;

^b extractable dissolved organic carbon;

^c hot-water soluble organic carbon;

^d KMnO_4 labile organic carbon;

^e total organic carbon;

^f total sulphur.

Table 2. Initial denitrification rates, long-term denitrification capacity, stock of reduced compounds, sulphate formation capacity and estimated minimal lifetime of denitrification (medians with ranges in brackets).

Data-set	$D_r(7)^a$ $\mu\text{g N}$ $\text{kg}^{-1} \text{d}^{-1}$	D_{cap}^b mg N kg^{-1} yr^{-1}	SRC^c	SRC_C^d	SRC_S^e	aF_{SRC}^f $\% \text{yr}^{-1}$ yr^{-1}	SFC^g mg S kg^{-1}	emLoD^h yrm^{-1}
				g N kg^{-1}				
FFA	33.8 (1.3–69.9)	15.1 (0.18–56.2)	0.70 (0.2–6.0)	0.67 (0.2–5.6)	50.50 (0.0–0.4)	1.5 (0.1–5.4)	5.3 (0–39.4)	5.3 (1.6–45)
GKA	31.16 (0.7–109)	9.6 (0.33–52.6)	1.10 (0.1–8.9)	0.75 (0.1–8.4)	0.36 (0.0–0.7)	0.8 (0.4–1.7)	4.2 (0–30.0)	8.3 (0.7–67)
non-sulphidic	11.5 (0.7–35.3)	1.6 (0.18–8.2)	0.24 (0.1–1.0)	0.22 (0.1–1.0)	0.03 (0.0–0.1)	0.47 (0.0–1.7)	0.3 (0–1.3)	1.8 (0.7–8)
sulphidic	35.6 (12.3–109)	15.6 (4.19–56.2)	1.3 (0.3–8.9)	1.04 (0.2–8.4)	0.32 (0.3–0.7)	1.16 (0.4–5.4)	8.1 (1.2–39)	9.7 (2.4–67)
transition zone	36.48 (20.3–61)	11.6 (7.8–17.2)	0.67 (0.3–1.6)	0.62 (0.3–1.5)	0.04 (0.0–0.1)	1.65 (0.6–4.6)	2.9 (1.5–7)	5.05 (2.5–12)
NO_3^- -bearing	21.05 (0.7–61)	4.3 (0.18–17.2)	0.54 (0.1–1.6)	0.50 (0.1–1.5)	0.035 (0.0–0.1)	0.80 (0.1–4.6)	1.0 (0–6.9)	4.1 (0.7–12)
NO_3^- -free	33.89 (12.3–109)	20.2 (4.0–56.2)	1.44 (0.3–8.9)	1.08 (0.2–8.4)	0.36 (0.0–0.7)	0.94 (0.4–5.4)	9.4 (0.7–39)	10.80 (2.4–67)

^a Initial denitrification rate after day 7;

^b long-term denitrification capacity;

^c stock of reactive compounds;

^d concentration of reduced compounds derived from measured C_{org} ;

^e concentration of reduced compounds derived from total-S values;

^f fraction of SRC available for denitrification during one year of incubation;

^g sulphate formation capacity;

^h estimated minimal lifetime of denitrification.

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Table 3. Spearman rank correlation coefficients between D_{cap} and sediment parameters for the full data-set and partial data-sets.

	$SO_4^{2-}_{extr}$	DOC_{extr}	C_{hws}	C_I	total-N	C_{org}	Total-S	Sand	Silt
Full data-set	-0.63 ^c	-0.59 ^c	0.36 ^a	0.68 ^c	0.55 ^c	0.72 ^c	0.64 ^c	-0.38 ^b	0.63 ^c
FFA	-0.82 ^c	-0.87 ^c	0.58 ^b	0.38 n.s.	0.34 n.s.	0.64 ^c	0.82 ^c	-0.44 ^a	0.64 ^c
GKA	-0.49 ^a	-0.40 n.s.	0.13 n.s.	0.87 ^c	0.78 ^c	0.88 ^c	0.88 ^c	-0.40 ^a	0.73 ^c
non-sulphidic	-0.38 n.s.	-0.53 ^a	0.85 ^c	0.73 ^b	0.32 n.s.	0.43 n.s.	0.65 ^a	-0.81 ^b	0.72 ^b
sulphidic	-0.45 ^a	-0.18 n.s.	0.24 n.s.	0.46 ^a	0.59 ^c	0.61 ^c	0.33 ^a	-0.28 n.s.	0.42 ^a
transition zone	-0.52 ^b	-0.59 ^b	0.60 ^c	-0.74 ^c	-0.59 ^c	-0.61 ^c	0.13 n.s.	-0.01 n.s.	0.52 n.s.

^a Correlation significant at the 0.05 probability level;

^b correlation significant at the 0.01 probability level;

^c correlation significant at the 0.001 probability level;

n.s. not significant.

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Table 4. Simple linear regressions between D_{cap} and $D_r(t)$, $f^{\text{B-C}}(D_{\text{cap}}) = A + B \times f^{\text{B-C}}(D_r(t))$.

Data-set	N^a	$D_r(7)$			$D_r(84)$			$D_r(168)$		
		R^b	A	B	R^b	A	B	R^b	A	B
full data-set	151	0.59	1.075	1.969	0.95	-0.361	0.962	0.96	0.065	1.085
FFA	86	0.57	2.005	2.705	0.94	-0.345	0.984	0.96	-0.015	1.123
GKA	65	0.68	1.613	2.565	0.94	0.452	1.503	0.94	-0.050	1.102
non-sulphidic	44	0.88	-0.391	1.264	0.95	-0.867	0.792	0.85	-0.216	1.160
transition zone	28	0.01	-3.866	-0.025	0.78	-1.556	1.156	0.69	-0.020	1.963
sulphidic	107	0.10	-2.521	0.304	0.82	0.047	1.697	0.91	1.326	2.514
NO_3^- -bearing	64	0.86	0.815	1.818	0.98	-1.446	0.427	0.94	-0.771	0.748
NO_3^- -free	87	0.15	-1.757	0.217	0.91	-0.613	0.750	0.94	0.183	1.394
FFA non-sulphidic	20	0.94	-2.125	0.239	0.97	-2.015	0.205	0.82	-1.527	0.441
FFA sulphidic	66	0.08	-1.928	0.880	0.82	-0.351	1.373	0.90	-0.462	0.785
GKA non-sulphidic	24	0.86	1.608	2.583	0.98	-0.546	0.926	0.87	1.007	1.877
GKA sulphidic	41	0.30	-1.684	1.028	0.86	2.147	2.863	0.91	2.353	3.343
FFA NO_3^- -free	38	0.58	-0.340	0.613	0.95	-0.754	0.675	0.89	0.027	1.279
GKA NO_3^- -free	49	0.31	-1.423	0.454	0.85	-0.462	0.808	0.93	0.125	1.374

^a Sample number;

^b correlation coefficient.

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Table 5. Results of multiple linear regression analysis between D_{cap} and various selections of sediment parameters. To achieve normal distribution, all variables in the different datasets were Box-Cox transformed. Regression coefficients are given for the equation $f^{\text{B-C}}(D_{\text{cap}}) = C_1 + C_2 \times f^{\text{B-C}}(\% \text{ silt}) + C_3 \times f^{\text{B-C}}(C_{\text{org}} \text{ mg kg}^{-1}) + C_4 \times f^{\text{B-C}}(\text{total-S mg kg}^{-1}) + C_5 \times f^{\text{B-C}}(\text{SO}_4^{2-} \text{ mg S kg}^{-1}) + C_6 \times f^{\text{B-C}}(\text{DOC}_{\text{extr}} \text{ mg C kg}^{-1}) + C_7 \times f^{\text{B-C}}(C_{\text{hws}} \text{ mg C kg}^{-1}) + C_8 \times f^{\text{B-C}}(C_1 \text{ mg C kg}^{-1})$.

Data-set	N^a	R^b	F^c	Regression coefficients							
				C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
Selection I: C_{org} und Total-S											
Whole dataset	151	0.82	153.1	-9.739	*	2.008	0.302	*	*	*	*
FFA	86	0.83	96.1	-17.950	*	1.366	5.565	*	*	*	*
GKA	65	0.86	85.6	-0.431	*	0.015	0.027	*	*	*	*
non-sulphidic	44	0.80	37.4	-204.2	*	0.586	247.877	*	*	*	*
sulphidic	107	0.66	40.5	-3.229	*	1.328	-5.0×10^{-5}	*	*	*	*
NO_3^- -bearing	64	0.71	30.3	-205.28	*	0.302	236.599	*	*	*	*
NO_3^- -free	87	0.80	76.9	-7.192	*	2.018	-0.003	*	*	*	*
transition zone	28	0.72	15.5	-446.52	*	-5.474	712.716	*	*	*	*
Selection II: two sediment parameters giving the highest correlation coefficient											
Whole dataset	111	0.86	154.1	-8.529	*	1.849	*	*	*	*	0.164
FFA	46	0.89	84.6	-18.935	*	*	7.553	-0.044	*	*	*
GKA	65	0.93	204.7	-5.326	*	1.274	*	*	*	*	0.204
non-sulphidic	44	0.80	37.4	-204.2	*	0.586	247.877	*	*	*	*
sulphidic	67	0.79	53.9	-6.399	*	2.254	*	*	*	*	-0.363
NO_3^- -bearing	56	0.80	51.2	-184.96	*	*	216.915	-0.191	*	*	*
NO_3^- -free	55	0.89	102.2	-9.437	*	2.963	*	*	*	*	-0.927
transition zone	20	0.74	12.8	193.30	*	-2.692	*	*	*	*	-181.402
Selection III: stepwise multiple regression with all sediment parameters											
Whole dataset	111	0.93	172.9	-0.090	*	1.415	*	-0.154	-3.169	*	0.146
FFA	46	0.95	105.9	0.466	-0.350	*	*	*	-0.309	0.299	0.166
GKA	65	0.97	188.4	-4.953	-0.545	*	0.014	-0.191	4.926	*	0.306
non sulphidic	44	0.96	122.7	-85.481	*	-0.525	*	*	-0.479	127.635	0.032
sulphidic	67	0.84	31.5	-6.166	-0.211	2.333	0.001	-0.091	*	*	-0.522
NO_3^- zone	56	0.93	112.0	2.589	*	*	*	-0.167	-0.142	*	0.240
NO_3^- -free	55	0.91	68.2	-8.581	*	2.581	0.003	-0.325	*	*	-0.754
transition zone	20	0.91	23.1	72.50	0.756	-18.033	*	-0.299	*	-0.186	*

*: Variable not included in the regression model;

^a number of included samples;^b correlation coefficient;^c f-coefficient.

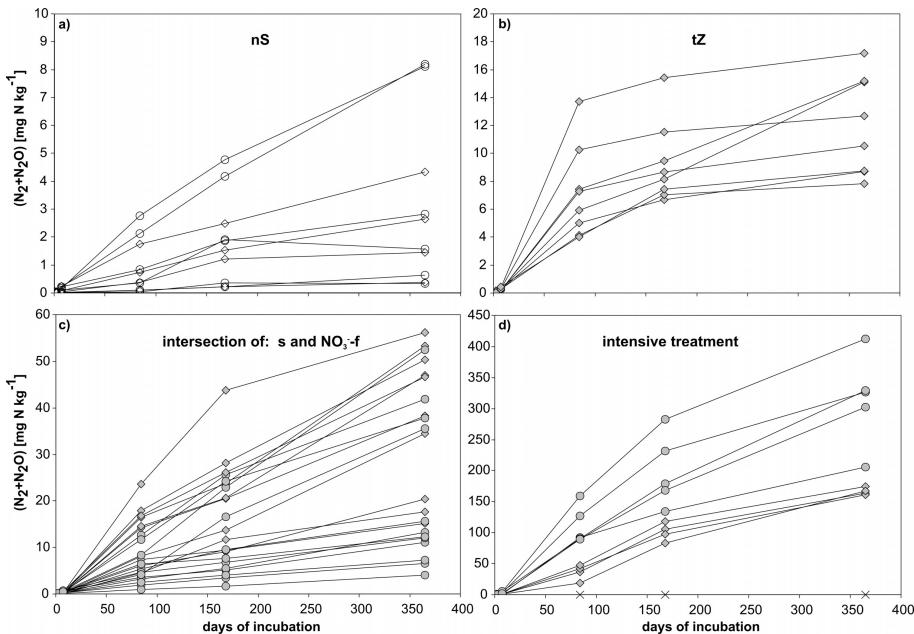


Fig. 1. Time courses of denitrification products ($N_2 + N_2O$) (average of 3 to 4 replicas per depth) from different groups of aquifer material during standard (**a** to **c**) and intensive treatment (**d**). Open and closed symbols denote non-sulphidic and sulphidic aquifer material, respectively. Circles and diamonds represent GKA and FFA material, respectively. Crosses indicate blanks of intensive treatment. nS, S, tZ and NO_3^- -f indicate non-sulphidic and sulphidic samples, transition zone material and NO_3^- -free samples, respectively. Error bars were omitted for clarity, but were small in comparison to measured concentrations of denitrified ($N_2 + N_2O$).

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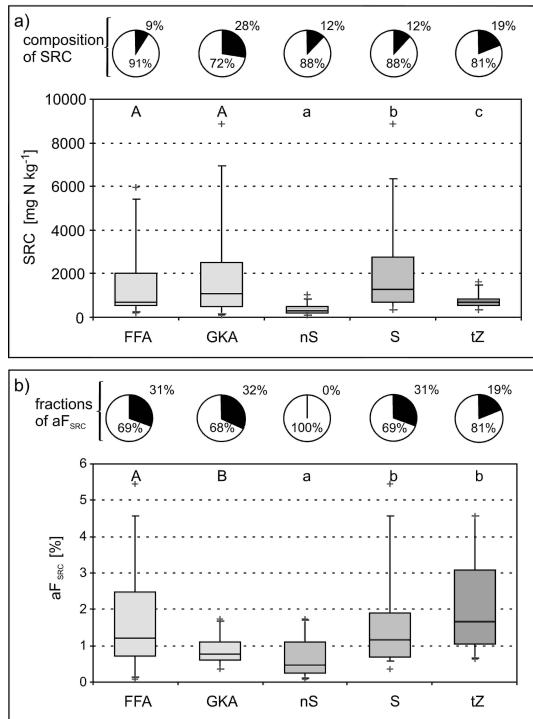


Fig. 2. FFA, GKA, nS, S and tZ indicate Fuhrberger Feld-, Großenketen-, non sulphidic-, sulphidic- and transition zone aquifer material, respectively. White circular segments represent fractions derived from C_{org} and black segments fractions derived from total-S values. Different uppercase letters above the box-plots indicate significant differences between FFA and GKA material, different small letters show significant differences between nS, S and tZ (Kruskal-Wallis-Test, $P < 0.05$). **(a)** The stock of reduced compounds (SRC) and its composition in the various groups of aquifer material. The composition of SRC was calculated from C_{org} and total-S values (Sect. 2.5). **(b)** Fraction of SRC available for denitrification during incubation (aF_{SRC}). The aF_{SRC} and its composition was calculated as described in Sect. 2.5.

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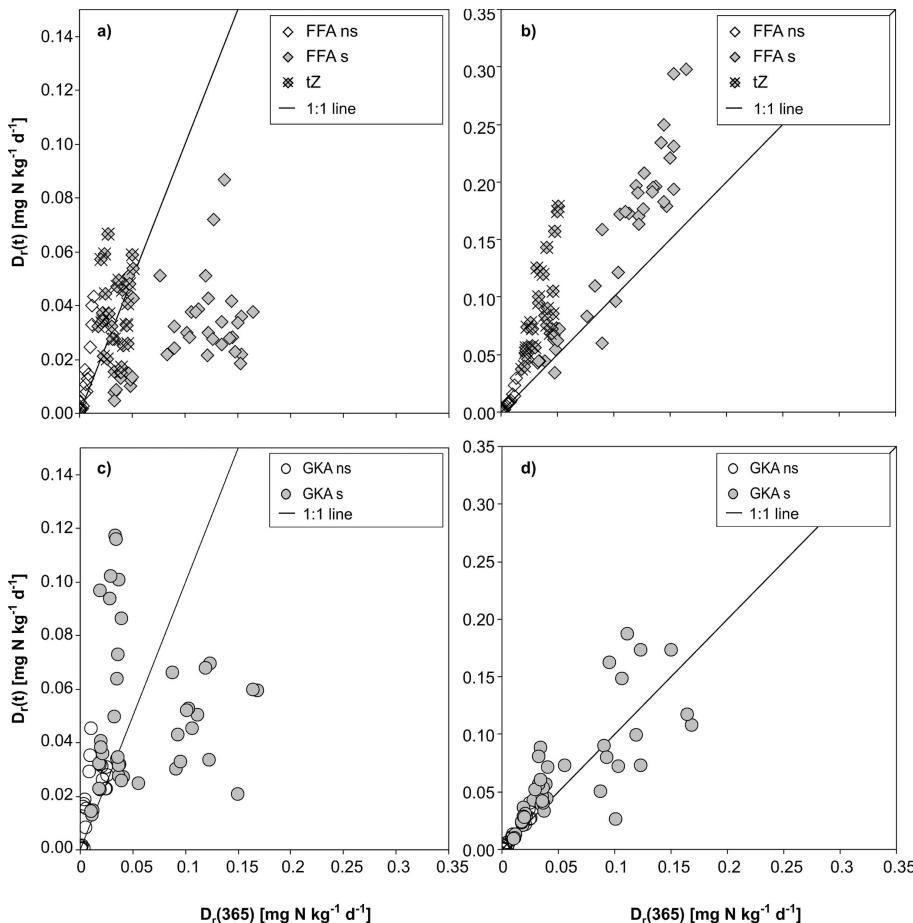


Fig. 3. Relation between denitrification rates determined during 7 ($D_r(7)$), 84 ($D_r(84)$) or 365 ($D_r(365)$) days of incubation. **(a)** $D_r(7)$ vs. $D_r(365)$ of FFA samples. **(b)** $D_r(84)$ vs. $D_r(365)$ of FFA samples. **(c)** $D_r(7)$ vs. $D_r(365)$ of GKA samples. **(d)** $D_r(84)$ vs. $D_r(365)$ of GKA samples.

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