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Measuring and modelling seasonal variation of gross nitrification rates in response to long-term fertilisation

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Abstract. The formation of nitrate (nitrification) in soils is an important process that influences N availability for plant uptake and potential N losses as well. Gross nitrification is an effective measure by which to test mechanistic ecosystem models for predictability because gross rates can widely differ between sites, even if net production is similar between these sites.

A field experiment was designed to (i) determine gross nitrification rates in response to fertilisation and (ii) to verify the idea that seasonal variations of gross rates in soils can be readily predicted by soil moisture and soil temperature.

Gross nitrification rates were measured by a Barometric Process Separation (BaPS). The BaPS measurements were validated with the commonly used ^{15}N pool dilution technique measurements at six times. In general, the rates determined from both measurement approaches were in the same order of magnitude and showed a good correlation.

The effects of 100 years of fertilisation (mineral fertiliser, manure and control) on gross nitrification rates were investigated. During 2004 soil samples from the long-term "static fertilisation experiment" at Bad Lauchstädt were sampled weekly and were measured in the laboratory under field conditions and subsequently under standardised conditions (16°C soil temperature and −30 kPa matrix potential) with the BaPS system. Gross nitrification rates determined under standardised conditions did not show any seasonal trend but did, however, reveal a high temporal variability. Gross nitrification rates determined by the BaPS-method under field conditions showed also a high temporal variability and ranged from 5 to 77 μg N h^{-1} kg^{-1} dry mass, 2 to 74 μg N h^{-1} kg^{-1} dry mass and 0 to 49 μg N h^{-1} kg^{-1} dry mass with respect to manure, mineral fertiliser, and control. The annual average was 0.34, 0.27 and 0.19 g N a^{-1} kg^{-1} dry mass for the manure site, mineral fertiliser site and control site, respectively. On all sites gross nitrification revealed a strong seasonal dynamic. Three different models were applied for reproducing the measured results. Test models could explain 75% to 78% of variability at the manure site, 66% to 77% of variability at the mineral fertiliser site, and 39% to 63% of variability at the control site. The model parameterisation shows that the temperature sensitivity of gross nitrification differs between the three neighbouring sites. Hence, a temperature response function in an ecosystem model has to consider the site specificity in order to adequately predict the effects of future climate change on the soil N cycle.

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1 Introduction

A firm understanding of the biogeochemical processes related to soil N cycling is important for developing mechanistic models which will prospectively allow a more reliable prediction of N gas emissions from agricultural soils (Murphy et al., 2007). Furthermore, biological nitrification is the key process by which N turnover and N removal from agricultural ecosystems occurs (e.g. Vitousek et al., 1979; Currie, 1996; Müller et al., 2004b; Cookson et al., 2006). Nitrification is known to promote nitrogen eluviation from soils, because the less mobile cation ammonium (NH_4^+) is oxidised by nitrifiers to the much more mobile anion nitrate (NO_3^-) (Abbasi and Adams, 1998). Also, nitrification is one of the main sources of nitrous oxide (N_2O) and nitric oxide (NO) released from agricultural soils (Russow et al., 2008), either directly as a by-product of nitrification (Firestone and Davidson, 1989), or indirectly through denitrification (Robertson and Tiedje, 1987; Khalil and Baggs, 2005). Therefore, biological nitrification is a crucial process which should be included in greater detail in the next generation of N cycle models.

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Numerous environmental parameters such as soil temperature, soil moisture, soil oxygen concentration, SOM content, NH_4^+ availability, pH-value etc. may act as important physiological constraints and therefore control nitrification rates in terrestrial ecosystems (Robertson and Tiedje, 1987; Booth et al., 2005; Cookson et al., 2006; Silva et al., 2005). In spite of the wide range of parameters that are potentially associated with nitrification rates, only some of them appear as model parameters.

Booth et al. (2005) for example, identified soil C and N content, NH_4-N availability, and N mineralisation as the best predictors for modelling nitrification. In addition, Cooksen et al. (2006) were able to demonstrate that from a total of 15 investigated soil parameters, soil moisture, soil temperature, NH_4^+ content, NO_3^- content, microbial N mass, microbial respiration rate, and dissolved organic N content were significantly correlated with the gross nitrification rate, whereby the best correlation was observed between gross nitrification rates and gross nitrogen mineralisation rates. Soil temperature and moisture may also be important for predicting soil nitrogen cycling. There may be a significant positive relationship between the soil temperature and nitrification rates (Breuer et al., 2002; Hoyle et al., 2006). Zaman and Chang (2004) also suggested a temperature dependency of the gross nitrification rate, but pointed out that in spite of moisture-induced variations in the nitrification rate, no consistent trend could be evidenced within a field capacity range of 50 to 100%. Considering the importance of temperature for N turnover in soils it is surprising that only a few studies have quantified the temperature dependency of the gross nitrification in soils (Murphy et al., 2003).

In addition to temperature, moisture may be an important indicator of soil nitrogen processes. There may be a negative relation between soil moisture and nitrification rate (tropical forest soils; Breurer et al., 2002). Zaman et al. (1999) demonstrated that the optimum soil water potential for gross nitrification rates was -10 kPa compared with -80 kPa and 0 kPa. Differences in nitrification rates at different water contents were more pronounced in the NH_4^+ fertilized treatment than in the unfertilized control (Zaman et al., 1999). Recous et al. (1998) investigated the influences of climate factors on gross N transformations in arable soils. They argued that the differences in gross nitrification observed at eight times between September 1993 and September 1994 could be explained by temperature and soil moisture conditions at each time. Jamieson et al. (1998) highlighted the problems of separating the direct impact of temperature and moisture from the indirect impact of changes of N- availability through mineralisation and consuming processes like microbial immobilisation and plant uptake.

Based on these previous studies, we hypothesised that soil temperature and soil moisture would explain most of the seasonal variation of gross nitrification in the field whereas soil organic matter (SOM) (Soil C and N content and NH_4^+-N availability) will be determined by the difference between the different sites. The main goals of this research were

1. to determine the influence of soil climate conditions on the gross nitrification at three differently fertilised sites
2. to confirm the effects of temperature and soil moisture by an additive manipulation experiment under standardised climate conditions
3. to parameterise model approaches which describe the temperature and soil moisture influence on gross nitrification in soils.

2 Materials and methods

2.1 Soil sampling

Soil sampling (5–10 cm soil depth) was carried out weekly (Mondays 09:00 to 12:00 h) over a period of one year (2004) at three differently treated agricultural sites (manure (D), mineral fertiliser (M), and control (C)) that form part of the long-term field study "Static Fertilisation Experiment" at the experimental research station of the Helmholtz Centre for Environmental Research – UFZ in Bad Lauchstädt. The soil was classified as Haplic Chernozem (Altermann et al., 2005). Manure fertiliser and mineral fertiliser is applied at a rate of 30 t farmyard manure ha^{-1} every second year (according to 96 kg N ha^{-1} a^{-1}) and 111 kg N ha^{-1} a^{-1}, respectively. The control site remained unfertilised since 1902. Intact soil cores (100 ml) were taken randomly from seven defined locations (sampling area 1 m^2) from each of the three agricultural sites. The soil temperature in the field was read from three permanently installed soil mercury thermometers at 5, 10, and 20 cm soil depth. The temperature at 10 cm soil depth was then used as the incubation temperature in the laboratory. Within 1 to 3 h sampled soil cores were transferred to the laboratory.

In order to determine ammonium and nitrate concentration, 25 g of soil fresh from the field was extracted with 100 ml 1M KCl and stirred on a rotary shaker for 1 h. The suspension was then filtered through a fluted filter (0.2 μm, Schleicher & Schuell, Dassel, Germany) and filtrate was analysed for NH_4^+ and NO_3^- with an auto-analyser (Bran & Lübbe, Germany).

At frozen soil conditions (2nd, 5th, 9th and 10th week) no soil sample was taken except at the 5th week. The frozen soil samples were very carefully transported to the laboratory to avoid thawing and to enable a measurement in the BaPS system in a frozen condition.

2.2 Gross nitrification rates determined by the BaPS

Gross nitrification rates were measured by the Barometric Process Separation (BaPS) system, which simultaneously determines denitrification and soil respiration rates. The determination of gross nitrification by BaPS technique is based

on the determination of the total pressure change, as well as the changes of O_2 and CO_2 partial pressure in an isothermal gas tight system. Nitrification leads to a pressure decrease by net oxygen consumption, denitrification leads to a pressure increase, and soil respiration is neutral for pressure (for a respiration coefficient RQ=1). The central equation of the BaPS method is

$$\Delta N_xO_y = \Delta n - \Delta O_2 - \Delta CO_2 \quad (1)$$

where ΔN_xO_y (mol h^{-1}) is the rate of N gases produced by denitrification. The symbol Δn (mol h^{-1}) denotes the net rate of total gas production ($\Delta n > 0$) or consumption ($\Delta n < 0$), and ΔCO_2 (mol h^{-1}) and ΔO_2 (mol h^{-1}) is the net rate of CO_2 formation and O_2 depletion, respectively, in the closed chamber's atmosphere. Since the total gas production (Δn), the net changes of O_2 (ΔO_2) and CO_2 (ΔCO_2) are measured, the production of N-trace gases (ΔN_xO_y) via denitrification can be calculated. The total O_2 consumption can be divided in three parts: 1) the O_2 consumption by respiration ($\Delta O_{2,R}$), 2) the O_2 consumption by nitrification ($\Delta O_{2,N}$), and 3) the change in the dissolved O_2 in soil water ($\Delta O_{2,aq}$):

$$\Delta O_2 = \Delta O_{2,R} + \Delta O_{2,N} + \Delta O_{2,aq} \quad (2)$$

Also the net CO_2 production can be expressed as

$$\Delta CO_2 = \Delta CO_{2,R} + \Delta CO_{2,N} + \Delta CO_{2,D} + \Delta CO_{2,aq} \quad (3)$$

where the indices R, N, and D refer to respiration, nitrification, and denitrification, respectively. The terms $\Delta O_{2,aq}$ and $\Delta CO_{2,aq}$ take into account that due to concentration changes during incubation, O_2 is released from soil solution to the chamber's atmosphere and CO_2 is transferred from the chamber's atmosphere to soil solution. In the BaPS system these terms are calculated using Henry's law.

By combining the total net gas balance equation (Eq. 1) with the O_2 and the CO_2 balance equations (Eqs. 2 and 3) and taking into the account that $-\Delta O_{2,R} = \Delta CO_{2,R}$ by a RQ of 1, nitrification can be calculated from the O_2 consumption for nitrifiers (mol h^{-1}) by

$$\Delta O_{2,N} = \frac{\delta}{\delta+1}\left(\Delta n - \Delta CO_{2,D} - \Delta N_xO_y - \Delta CO_{2,aq} - \Delta O_{2,aq}\right) \quad (4)$$

where δ stands for the $\Delta O_{2,N}$ to $\Delta CO_{2,N}$ ratio, which is a fixed value of 7.3. Further details including discussion of uncertainties are given by Ingwersen et al. (1999, 2008), Breuer et al. (2002) and Müller et al. (2004a).

Fresh soil cores from the field were stored in the BaPS system, acclimatised to temperature and moisture corresponding to field sampling condition for 2 to 38 h, and then (still at field conditions) run for 8 to 16 h on the BaPS to determine gross nitrification rates. Afterwards the BaPS measurement was repeated under standard conditions (16°C soil temperature, −30 kPa soil matrix potential). For this purpose soil cores were removed from the BaPS system and drained for 5 days by putting them on a ceramic plate at −30 kPa under pressure. If necessary, soil samples were also moisturised with N-free standard rain prior to drainage. Drained soil cores were then put back into the BaPS system and acclimatised for 2 to 38 h at 16°C before measurement.

At each step the water content was controlled gravimetrically and calculated after drying for 24 h at 105°C at the end of all measurements.

The calculation of gross nitrification, denitrification and soil respiration rates was carried out by using the original BaPS software (UMS, München, Germany), taking into consideration a shortcoming in the calculation of the carbonate equilibrium as published recently by Ingwersen et al. (2008). The ratio of autotrophic nitrification to total nitrification was set to 1, as nitrification can be assumed to be predominantly carried out by autotrophic nitrifiers (Stange and Döhling, 2005). The ratio between N_2O- and N_2-production by denitrification was set to 1:3 for this soil according to Wolf and Russow (2000).

2.3 Gross nitrification rates determined by the ^{15}N pool dilution technique

For comparison purposes, ^{15}N pool dilution (Kirkham and Bartholomew, 1954) was conducted simultaneously with the BaPS approach at 6 randomly selected points in time over the 2004 study period. In this context seven fresh soil cores from the field were broken down carefully by hands (protected with gloves) in small aggregates (<6 mm) and 20 ml ^{15}N solution (5 mM $K^{15}NO_3$ 95.8 at%) was added by spraying. During the labelling procedure the soil was simultaneously mixed several times to ensure a homogenous labelling with ^{15}N. Afterwards soil aggregates were refilled in the seven steel cores and placed in the BaPS system for acclimatisation. In order to determine the initial ^{15}N abundance of labelled soil NO_3^-, one soil core was removed from the BaPS system 6 h after ^{15}N labelling and extracted as describe below. The remaining soil cores were measured three times with the BaPS system for a period of 12 h at 16°C. Soil extraction was then repeated with one soil core as follows. PE flasks were each filled with 25 g of fresh soil and 100 ml 1M KCl solution was added. The samples were stirred on a rotary shaker for 1 h and the suspension was filtered through a fluted filter (0.2 μm, Schleicher & Schuell, Dassel, Germany). ^{15}N-NO_3^- abundance and NO_3^- concentration in the extracted soil solution was determined by SpinMas (Stange et al., 2007). A subsample of each of the remaining 5 soil cores were used to determine the soil water content.

2.4 Statistical analysis

Statistical analyses were performed using the STATISTICA 8.0 software. Analyses of variance between the different treatments were conducted using T- tests. The coefficient of variation (CV), defined as the standard derivation (SD) divided by the mean value, was used to compare the variation of measurements by different means.

2.5 Model approach

To determine the effects of soil temperature, water content, and possible interactions between these two factors on nitrification rates, three approaches were tested and parameterised based on the experimental results:

1. the climatic factor proposed by Andrén and Paustian (after Recous et al., 1998) was used. The model is based on the exponential relationship between nitrification rates and temperature and soil water potential. Soil water potential in field samples was estimated from the water content using a retention curve. The reference temperature used here was 10°C. The parameters were recalculated by multiple regression using STATISTICA.

2. A multiple linear regression with two factors (soil temperature and soil moisture) was used. For temperature the incubation temperature of the BaPS system was used, and for soil moisture the measured gravimetric water content was used.

3. A two-factor model as described by Stange (2007) was used. Two different functions to describe the temperature response were tested (i.e. the Arrenius function, and the optimum function from O'Neill). The best results were obtained if the O'Neill function:

$$f(T) = \left(\frac{T_{\max} - T}{T_{\max} - T_{\text{opt}}}\right)^{a} * e^{a * \frac{T - T_{\text{opt}}}{T_{\max} - T_{\text{opt}}}} \quad (5)$$

with $f(T)$ effect of soil temperature 0–1 [], T soil temperature [°C], $T_{\max}$ maximum temperature of the O'Neill function, fixed at 40°C, T_{opt} optimal temperature of the O'Neill function [°C], a shape parameter of the O'Neill function [] was used to calculate the temperature response. The soil moisture response was described with the following function:

$$f(M) = 1 - e^{-\left(\frac{M}{M_{\text{crit}}}\right)^{b}} \quad (6)$$

with $f(M)$ effect of soil moisture on gross nitrification 0–1; M soil water content [% g water g^{-1} soil]; M_{crit} critical water content [% g water g^{-1} soil]; b sharp parameter of the function [].

For combining the temperature and moisture response functions, the mathematical approach published by Stange (2007) was used. It is the harmonic mean and is driven by the idea of a limiting factor as given by the Liebig's law:

$$g(f(M), f(T)) = \frac{2 * R_{\max}}{\frac{1}{f(T)} + \frac{1}{f(M)}} \quad (7)$$

with g response function; $R_{\max}$ maximal nitrification rate [μg N kg^{-1} h^{-1}]; f response functions for each factor (e.g., temperature or moisture).

Estimates of parameters for gross nitrification were conducted using the non-linear parameter estimate procedure in STATISTICA 8.0.

3 Results

3.1 Site description

The soil was classified as Haplic Chernozem (Altermann et al., 2005). Its loess substrate comprises 21% clay, 68% silt, and 11% sand. Collected soil had a total N (N_t) of 0.19, 0.16 and 0.13% and a total carbon (C_t) content of 2.3, 1.9 and 1.6% for manure (D), mineral fertilisation (M), and the control (C), respectively. Soil pH in distilled water, from air-dried, sieved (2 mm) soil ranged from 6.6 to 6.9, 6.5 to 6.7, and 7.4 to 7.8 for D, M, and C, respectively. Detailed information on this soil type is provided by Altermann et al. (2005).

3.2 Comparison of BaPS and the ^{15}N pool dilution technique

In general, the gross nitrification rates calculated using the BaPS system showed a good correlation compared to values determined by the ^{15}N pool dilution technique (r^2 0.78, 0.95, and 0.88 for manure, mineral fertilisation, and the control, respectively). Both methods revealed strong variations for the gross nitrification rates determined. The CV for standardised gross nitrification rates measured by the BaPS system was 0.22 whereas the CV for standardised gross nitrification rates determined by the ^{15}N pool dilution technique was 0.30. Beyond these fairly large variations in gross nitrification rates between both methods, it should be noted that considering the manure site, gross nitrification rates calculated by the ^{15}N pool dilution technique on average were 30% lower than the rates determined by the BaPS system (Fig. 1).

3.3 Gross nitrification rates on the three differently treated agricultural sites

3.3.1 Under field conditions

With respect to the annual course, a distinct seasonal trend with maximum gross nitrification rates during summer and minimum rates in the winter was observed at all three sites. In general the lowest gross nitrification rates were determined under frozen conditions at the beginning of February, whereas the highest rates were observed between calendar week 20 and 29 (10 May to 12 July).

Gross nitrification rates under field conditions determined by the BaPS system ranged from 5 to 77 μg N h^{-1} kg^{-1} dry mass, 2 to 74 μg N h^{-1} kg^{-1} dry mass, and 0 to 49 μg N h^{-1} kg^{-1} dry mass for the manure site, mineral fertiliser site, and the control, respectively. On average the highest gross nitrification rate was found at the site fertilized with manure (38±21 μg N kg^{-1} h^{-1}), whereas the lowest mean gross nitrification rate was found at the unfertilised control site (22±13 μg N kg^{-1} h^{-1}). The mineral fertilizer site showed a mean gross nitrification rate of 31±18 μg N kg^{-1} h^{-1}. The

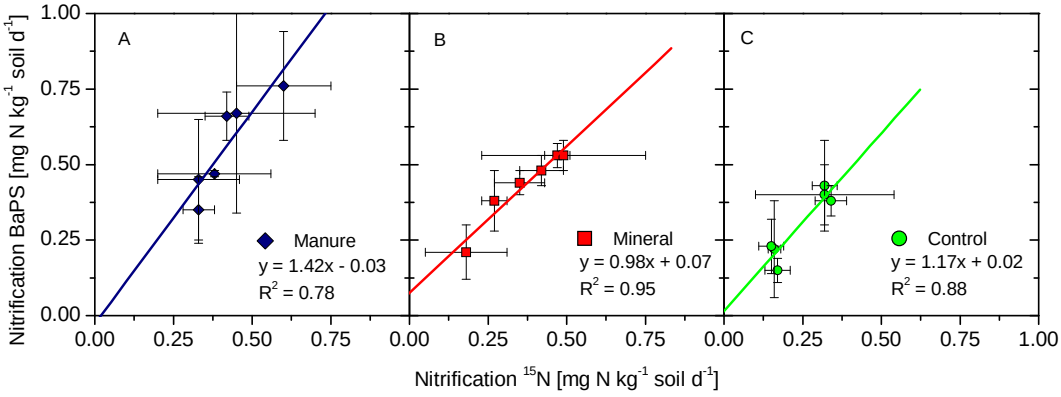

Fig. 1. Comparison of gross nitrification rates measured with the BaPS and the ^{15}N pool dilution technique for the three field sites **(a)** manure fertiliser, **(b)** mineral fertiliser, and **(c)** control (without fertiliser). Parameter of the linear regression and the r^2 value are given in the figures.

observed differences between the sites are statistically significant (t-test, $p<0.01$) and mean nitrification rates are linearly correlated with field C_t and N_t values. The coefficient of variation (CV) was comparable on the three sites with 0.54, 0.58, and 0.58 for the manure site, mineral fertiliser site, and the control, respectively. Average ammonium concentration in the soil was 1.6, 1.6, and 1.0 mg NH_4^+-N kg $^{-1}$ dry mass for D, M, and C, respectively. Consequentially, the minimal mean residence time (MRT) of ammonium during nitrification at these sites is around 20 h.

3.3.2 Under standard conditions

Gross nitrification rates under standard conditions (16°C and −30 kPa matrix potential) (Fig. 3) ranged from 30 to 83 μg N h^{-1} kg^{-1} dry mass, 19 to 67 μg N h^{-1} kg^{-1} dry mass, and 18 to 53 μg N h^{-1} kg^{-1} dry mass with respect to the manure site (D), the mineral fertiliser site (M), and the control site (C). Further, mean gross nitrification rates were 49±12 μg N h^{-1} kg^{-1} dry mass, 43±10 μg N h^{-1} kg^{-1} dry mass, and 31±8 μg N h^{-1} kg^{-1} dry mass for D, M, and C, respectively. High variations in the nitrification rates were observed at each site but the CV were almost equal between the three sites ranging from 0.24 to 0.25. As expected the observed CV under standard conditions were clearly smaller than in the measurements under field conditions. A small seasonal trend was only visible with respect to the control site. For the fertilised plots no clear trends or seasonality was observed.

3.4 Modelling gross nitrification rates

Three different models were tested to explain the seasonal variability in gross nitrification rates in the field. Multiple linear regression analyses explained seasonal variability in the gross nitrification rates with 76%, 75%, and 48% for the manure site (D), the mineral fertiliser site (M), and the control (C), respectively. The new parameterised approach developed by André and Paustian (Recous et al., 1998; Ambus, 2005) explained 78%, 72%, and 39% (M, D, and C, respectively) of the variability due to soil temperature and soil moisture.

The approach we propose here (Eqs. 5 to 7) explained 63 to 78% of the observed variations (Table 1). Measured and simulated mean values were almost equal (D: 38.4 μg N h^{-1} kg^{-1} dry mass vs 38.3 μg N h^{-1} kg^{-1} dry mass; M: 30.5 μg N h^{-1} kg^{-1} dry mass vs. 30.5 μg N h^{-1} kg^{-1} dry mass; C: 22.0 μg N h^{-1} kg^{-1} dry mass vs. 22.0 μg N h^{-1} kg^{-1} dry mass for both simulated and observed mean values, respectively). Nevertheless, the CV of the simulated gross nitrification rates (D: 0.49, M: 0.51, C: 0.49) was smaller than for those of the observed rates on all sites.

3.5 Respiration rates under field conditions

Respiration rates from the three different fertilised sites showed a strong seasonality, with maximum rates during the late spring and minimum rates in the winter (Fig. 4). Highest respiration rates was observed between week 21 and 23 in the fertilised sites and in week 28 at the control site with maximal rates of 351, 275 and 262 μg C kg^{-1} h^{-1} for D, M, and C, respectively. On average the lowest respiration rates were determined at the unfertilised control site (65±68 μg C kg^{-1} h^{-1}), the highest at the site fertilized with manure (119±103 μg C kg^{-1} h^{-1}), and intermediate rate were found at the mineral fertilised site (91±82 μg C kg^{-1} h^{-1}).

4 Discussion

4.1 Comparison of the BaPS method and the ^{15}N pool dilution technique

To the best of our knowledge this was the first extensive validation ^{15}N pool dilution versus BaPS respect to agriculturally-used soils other than a two point validation published recently (Ingwersen et al., 2008). In general a

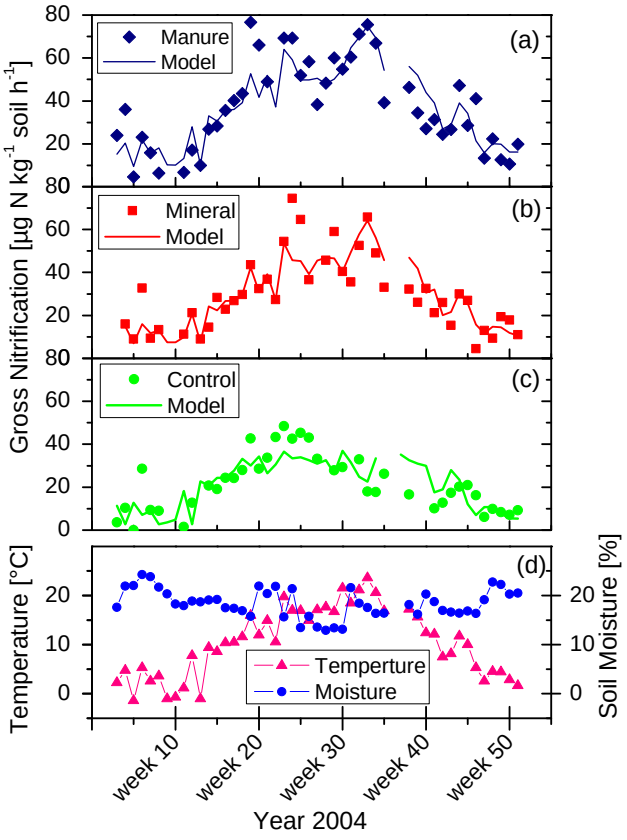

Fig. 2. Comparison of simulated and gross nitrification rates measured with BaPS on the three sites **(a)** manure, **(b)** mineral fertilised, and **(c)** the control (unfertilised for over 100 years). **(d)** Seasonal variation in the soil temperature and soil moisture (averaged value for the three sites) in 2004.

good correlation was observed between the BaPS and ^{15}N pool dilution measurements (r^2 0.78, 0.95, and 0.88 for D, M, and C, respectively). Notably, the gross nitrification rates calculated using the BaPS system depend greatly on the input parameter soil pH-value. The pH-values were measured in water after conducting the BaPS measurement, but were not determined in situ during the experiments. Ingwersen et al. (2008) pointed out that BaPS nitrification rates using the current pH value (measured in water) conformed better with the ^{15}N pool dilution technique measurements than BaPS calculations using potential pH values (measured in CaCl solution). Soil pH values measured using both methods can strongly differ i.e. in the investigated soil by up to 0.5 pH units (Altermann et al., 2005), which leads to differences of up to 50% in the calculated gross nitrification rates in alkaline soils (Ingwersen et al., 2008). This can be observed in particular for the control site where the soil pH value ranged between 7.4 and 7.8 (measured in water) and thus might be responsible for differences in gross nitrification rates determined by the BaPS approach and the ^{15}N pool dilution technique, respectively. One of the general assumption of the

Table 1. Model parameters used for the simulation of gross nitrification and the resulting coefficient of determination.

	R_{max} [μg N kg^{-1} soil h^{-1}]	T_{opt} [°C]	a [ ]	M_{crit} [g water g^{-1} soil]	B [ ]	r^2
Manure fertiliser	84	28	2.4	0.12	2.0	0.775
Mineral fertiliser	72	30	1.8	0.10	16	0.755
Control	39	18	14.6	0.15	3.0	0.633

BaPS approach is that mineralisation, nitrification, and denitrification are the only processes involved in the gas household in the enclosed soil system (Ingwersen et al., 1999). We tested this assumption by measuring the methane emission or uptake and possible N_2 fixation by free living diazotrophs. There was no significant change in the methane concentration between the beginning and the end of the BaPS incubation (not illustrated) and the $^{15}N_2$ uptake was smaller than the detection limit. This suggests that the impact of both gases was negligible for the BaPS determination in this soil.

Differences between the two methods are also explainable by uncertainties in the gross rate determination by the ^{15}N pool dilution technique. This technique is based on a number of assumptions: (1) no isotopic discrimination, (2) no re-mineralisation of added labelled N, (3) constant process rates during incubation, and (4) similar behaviour of added and native N pools (Murphy et al., 2003). We paid specific attention to distributing the ^{15}N as uniformly as possible, by using well homogenised soil and by adding the ^{15}N solution through spraying. However, a completely homogenous mixture of the isotope with the soil inorganic N pool was virtually impossible. Given the heterogeneity of soils it is highly unlikely that the applied $^{15}NO_3^-$ will generate an immediate equilibrium with the indigenous soil nitrate. Recent investigations challenged the one pool theory (Stevens et al., 1997; Spott et al., 2006), and at least for NO_2^- more than one pool was proven in this soil (Russow et al., 2009). Mathieu et al. (2007) found that isotopic fractionation can be neglected if enrichment is higher than 0.6%, as it was the case in this study.

The observed high variation in the nitrification rates compared to other studies using BaPS could be explained by the low nitrification rate in these soils. Nitrification rates in this study were in the range of BaPS measurements from two other agricultural soils (Ingwersen et al., 2008) but were one order lower than BaPS measurements determined in forest soils (Ingwersen et al., 1999; Breuer et al., 2002; Stange, 2007) or in an old grassland soil (Müller et al., 2004a). The BaPS system was developed for forest soils, especially for the litter layer where a high turnover rate was observed (Ingwersen et al., 1999). Therefore we tested the BaPS system without soils and with PVC dummies. In these cases

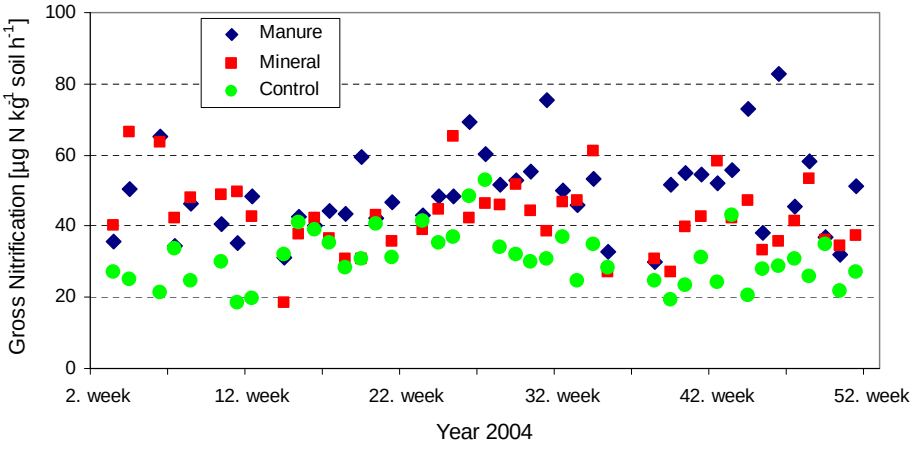

Fig. 3. Measured nitrification rates on the three sites manure, mineral fertilised, and the control (unfertilised for over 100 years) under standardised conditions (16°C, −300 hPa).

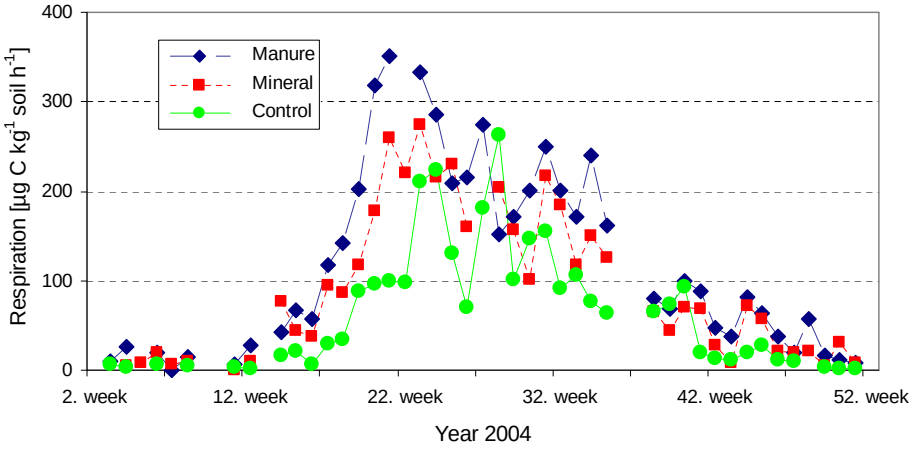

Fig. 4. Measured respiration rates from the three sites each of manure, mineral fertilised, and control (unfertilised for over 100 years) in the BaPS under field conditions.

no change in the O_2, CO_2, or absolute pressure were observed. Considering our extensive validation and previously published studies we conclude that the BaPS system is an appropriate method to determine gross nitrification rates, in particular if differences between sites and the variation in time are in the focus of interest. Nevertheless, in mineral soils its applicability to measure nitrification rates is limited to the soil surface.

4.2 Gross nitrification rates under field conditions

Gross nitrification rates of the three treatments were similar to nitrification rates calculated from nitrate concentration and ^{15}N abundance reported by Russow et al. (2008). For the first 3 day interval the nitrification rate was 54 μg N kg^{-1} h^{-1} (soil temperature: 19–21°C, soil moisture: 0.20 to 0.22 g H_2O g^{-1} dry soil). Gross N mineralisation calculated from the ^{15}N ammonium experiment was 189 μg N kg^{-1} h^{-1} (soil temperature: 16–18°C, soil moisture: 0.20 g H_2O g^{-1} dry soil). Nevertheless, average rates (38, 31, and 21 μg N kg^{-1} h^{-1}) were lower compared to former studies with other soils (Table 2). This might be caused by lower mean temperatures as published in previous studies. Furthermore, most of the former studies focused directly on the influence of nitrogen addition on nitrification rates and thus higher rates can be expected (Murphy et al., 2007).

A clear response to soil temperature was observed in the measurements under field conditions. However, the highest nitrification rates were not observed at the highest temperatures. During the interval of the highest temperatures (calendar week 30 to 34) the nitrification rate was possibly limited by substrate supply. No indication of limited substrate (predominantly NH_4^+ supply) was given in these samples during the measurements under standard conditions following the measurements at field condition. Therefore, it must be concluded that if a substrate limitation caused

Table 2. Summary of published gross nitrification rates in agricultural soils. [a] Standardised condition 16°C and field capacity (FC) (−6 to −30 kPa matrix potential).

Author	Region	Location	Culture	Treatment	Additional variations	Rates [μg N kg^{-1} h^{-1}]				comment
						Min	Max	(16°C, FC)[a]	mean rate	
Cookson et al. (2006)	Australia	field	wheat	organic	Variation in soil moisture and temp.	19	119		62	four times in the vegetation period
				biodynamic	Variation in soil moisture and temp.	23	123		65	four times in the vegetation period
				Integrated	Variation in soil moisture and temp.	15	123		69	four times in the vegetation period
				conventional	Variation in soil moisture and temp.	21	167		89	four times in the vegetation period
Hoyle et al. (2006)	western Australia	lab	wheat/legume	with stubble	Temperature range 5°C to 40°	33	246	63	113	
				stubble burnt	Temperature range 5°C to 40°	29	183	46	75	
Ambus (2005)	Danmark	field	grass-clover pasture 1-year-old	Moisture between 59–69%WFPS		142	229		172	four times in the vegetation period
				2-year-old	Moisture between 53–68%WFPS	125	233		192	four times in the vegetation period
				8-year-old	Moisture between 56–72%WFPS	96	358		203	four times in the vegetation period
Silva et al. (2005)	Oklahoma	field	old grass-land	Temperature 20–29°C	Moisture 24.5–32%	8	58		28	five times in the vegetation period
Khalil et al. (2004)	France	lab	maize	0 kPa O2		0	0		0	five measurements over the time
				0.35 kPa O2		50	71		64	five measurements over the time
				0.76 kPa O2		113	175		139	five measurements over the time
				1.5 kPa O2		150	350		254	five measurements over the time
				4.3 kPa O2		179	642		367	five measurements over the time
				20.4 kPa O2		29	633		394	five measurements over the time
Zaman and Chang (2004)	Australia	lab	agroforestry	bare ground	temperature 5°C to 40°, Moisture 50–100% FC	9	55	31	33	
				ryegrass	temperature 5°C to 40°, Moisture 50–100% FC	15	123	62	69	
				Lucerne	temperature 5°C to 40°, Moisture 50–100% FC	24	138	76	92	
Cookson and Murphy (2004)	western Australia	lab	pasture	control	sandy loam/sandy clay loam	142	271		206	incubated at 20°C, 75 FC
				without DOM	sandy loam/sandy clay loam	79	142		110	incubated at 20°C, 75 FC
Cooksen et al. (2002)	New Zealand	lab	cereal	control	Temperature range 2°C to 15°	4	119	65	48	15 observations in 160 days
				clover added	Temperature range 2°C to 15°	21	717	305	214	15 observations in 160 days
Recous et al. (1999)	France	field		control	Temperature 4.4–20.5°C Moisture 19.7–28.5%	35	150	55	78	eight times in the vegetation period
				straw amended	Temperature 4.4–20.5°C Moisture 19.7–28.5%					eight times in the vegetation period
Zaman et al. (1999)			control	0 kPa	control, dairy shed effluent and NH4+ added	13	40		22	six observations in 90 days
				−10 kPa		25	52		42	six observations in 90 days
				−80 kPa		27	46		37	six observations in 90 days
Watson and Mill (1998)	Northern Ireland	lab	grassland	100 kg N ha^{-1} a^{-1}					112	15°C, 38.2% H2O/DM
				200 kg N ha^{-1} a^{-1}					214	
				300 kg N ha^{-1} a^{-1}					272	
				400 kg N ha^{-1} a^{-1}					421	
				500 kg N ha^{-1} a^{-1}					462	
					MEAN	53	206	88	148	

these lower rates, ammonium consumption (e.g. uptake by heterotrophic microorganisms or plants) is more temperature sensitive at high temperatures than ammonium production (N-mineralisation). It should be considered that processes in the N-cycle of soils (e.g. N-mineralisation, nitrification, and NH_4^+- and NO_3^- immobilisation) are closely linked together (Corre et al., 2002) and therefore it is difficult to separate the direct and indirect impact of climatic factors on the process of the N cycle (Jamieson et al., 1998). The short mean residence time (MRT) for NH_4^+ in our soil demonstrates that NH_4^+ availability is determined more by N-mineralisation than by the size of the NH_4^+ pool in the soil. Therefore the response of measured actual nitrification rates on temperature is an "apparent" temperature sensitivity. Davidson and Janssens (2006) concluded that the "apparent" temperature sensitivity of microbial soil processes underestimates the intrinsic sensitivity of nitrification to low substrate concentrations.

Also other studies found a decreasing Q_{10} value with increasing temperature or even a decrease in gross nitrification rates at higher temperatures when the chosen temperature interval was large (e.g. Zaman and Chang, 2004; Stange, 2007).

Normally, the optimal temperatures for microbial processes in the field are adapted to the maximal temperatures in the field (Malhi and McGill, 1982; Stark and Firestone, 1996). Following the hypothesis that microorganisms are adapted to their optimal temperature range at the climate conditions of their habitat (Nozhevnikova et al., 2001; Fierer et al., 2003), we must expect similar intrinsic temperature sensitivity for the three sites. The optimum temperature found on the control site, however, was unexpectedly low (17°C) in this study. These findings contradict the observation made by Recous et al. (1998) who observed the highest nitrification rate at the highest temperature (20.4°C) and a strong temperature response in the interval from 4°C to 21°C (a Q_{10} value 3.17). If limited substrate availability is the reason for stunted rates at higher temperature then the strongest influence should be observable at the unfertilised control site, as found in our results. Nevertheless, the observed shift in the optimal temperature from near 30°C at the fertilised plots to 17°C at the unfertilised plot is much stronger then actually expected when following the hypothesis from Davidson and Janssens (2006).

In the interval between 0 and 16°C the temperature sensitivity at the unfertilised control plot is higher then at the fertilised plots, which is consistent with the Arrhenius equation. Due to the fact that higher activation energies are necessary to degrade substrates with "lower quality", the temperature sensitivity increases when substrates with "lower quality" are used (Davidson and Janssens, 2006). However, this theory can be only valid for N-mineralisation, since the N-substrate for nitrification (NH_4^+) doesn't change quality. If nitrification is closely linked to N-mineralisation it is possible that the "apparent" temperature sensitivity for nitrification as shown in this study is dominated by the temperature sensitivity of N-mineralisation. Fierer et al. (2005) pointed out, that Q_{10} values can shift from 2.3 to 3.0 caused by an altering of the substrate for mineralisation due to preferential mineralisation of organic matter with high quality at the beginning of incubation.

Nevertheless the model can only explain 63% of the observed temporal variation at the control site the highest uncertainties must be expected at this site because the low nitrification rates. The goodness of parameter estimation decreased only slightly if the parameter T_{opt} was fixed to 30°C. Therefore, the optimum temperature (T_{opt}) found at the control site is influenced by the high uncertainty of gross nitrification rates

Decreasing soil water content was observed at two periods in the summer. The first period in particular, when soil moisture fell below 0.16 g H_2O g^{-1} dry soil, a decrease in the gross nitrification rates was measured. Nevertheless, the influence of soil moisture is much smaller than the influence of temperature (Recous et al., 1998). Our results illustrated that microbial activity is only affected in extreme dry or wet conditions, and has a wide interval of soil moisture where moisture is not limiting. However, 2004 was not a dry year and it should be considered that no strong moisture changes could be observed in 2004. The lack of extreme dry conditions may explain some of the distinct uncertainties with respect to soil moisture response. Laboratory studies with manipulated soil moisture have found increasing nitrification with increasing soil moisture (e.g. Khalil and Baggs, 2005), as is expected in microbial processes, if O_2 availability is not limited.

4.3 Gross nitrification rates under standard conditions

Observed nitrification rates under standard conditions averaged 49, 43, and 31 μg N kg^{-1} h^{-1} and are in the range observed by other studies at similar soil temperature and soil moisture conditions (see Table 2). The measurements showed great variation with CV's between 0.24 and 0.25. The CV of measurements under standard conditions was only marginally higher than the CV in the BaPS measurements due to the BaPS validation against the ^{15}N pool dilution technique (CV: 0.22). It is assumed that this CV is due to the uncertainties in the BaPS measurement system. Therefore most of the observed variability over the time in the measurements under standardised condition (0.24 and 0.25) is likely caused by uncertainty of the BaPS system rather than by seasonal variation. The poor seasonal trend with respect to the control site is likely because of lower nitrification rates in the first ten weeks. The comparability of gross nitrification measurements under field and standard conditions was illustrated by the similar measured rates under standard condition and calculated rates from the model approach. This comparability of the measurement results under field conditions (measured

4 to 40 h after sampling) and standard conditions (including a one-week storage in the laboratory to adjust the matrix potential to −30 kPa) confirmed our assumption, that the nitrification rate is not altered too much by storage.

4.4 Modelling gross nitrification rates

With the exception of modelling the measured nitrification rate at the control plot, all of the tested approaches could explain the variation with a very similar accuracy. This is probably due to the fact that our proposed approach differs more from conventional approaches under extreme conditions than close to the optimum. On the control plot the differences in the approaches could be explained by measured nitrification rates not increasing at temperatures over 20°C. We can therefore conclude that the combined approach from Stange (2007) led to no better results than the classical multiplying approaches using the climatic factor and the multiple regression. Changing the response function for temperature (Arrhenius vs. O'Neill function) definitely has more of an effect than changing the combining approach. The "apparent" temperature sensitivity is better described by the O'Neill function, especially on the control plot where the nitrification rate decreased at temperatures over 20°C. Compared to the more common Arrhenius function, the O'Neill function is an optimum function and does not work at temperatures over the parameter $T_{\max}$. This function is more suitable in characterising microbiological processes at high temperatures than the monotonically increasing Arrhenius function which was developed for chemical reactions. In this study the O'Neill function was used because many investigations dealing with a temperature response observed a decrease in the Q_{10} value or gross nitrification with an increasing temperature with a high temperature interval (e.g. Zaman and Chang, 2004; Stange, 2007). Nevertheless, at low temperatures both the O'Neill and the Arrhenius function act very similar and a proxy Q_{10} value can be deviated from both. Therefore in general these results are in agreement with the results from Recous et al. (1998) who investigated the nitrification rate for a small interval from 4°C to 21°C and found a strong temperature response with a Q_{10} value of 3.17.

Even more differences than between the model approaches were observed between the three sites. It was assumed that climatic conditions were the same on all plots over the 100 years of different fertiliser management, because the plots are a maximum of 150 m from each other. Parameters of the soil moisture function are uncertain however, caused by the small variability of soil moisture observed in the field in 2004.

To compare the coefficient of variation of measurements under field conditions with the measurements at standardised conditions the climatic influence was eliminated. For this model results were normalised by the measurements under field conditions, e.g. if the climate factor explained all of the variations in the measurements the normalised nitrification was 1 for each day and consequently the CV was 0. The CV of the normalised measurements were 0.33, 0.32 and 0.37 for D, M and C, respectively, and consequently higher than the CV of measurements under standardised conditions (0.25 and 0.24). Since these observations can not confirm the mineralisation results of the BaPS based on the same samples, we would not overrate these findings.

4.5 Respiration rates under field conditions

Between 64% (mineral fertilised site) and 68% (the other both) of the variation in the soil respiration rate can be explained with the temperature response function of O'Neill. The inclusion of soil moisture has only a small impact and increases only marginal this number to 65 to 68%. However, highest respiration rates were observed in the late spring, where plant growth was high, not at the time of highest temperatures. Therefore it is believed that root exudates and easily mineralisable plant residuals are more available at this time than in the summer with the highest temperature. Consequently the respiration in summer may be limited by substrate supply. The influence of substrate limitation was intensively discussed in Sect. 4.2 and by Davidson and Janssens (2006). Respiration rates determinate with the BaPS were comparable with the results of an earlier study on these sites by Klimanek (2000). Klimanek (2000) reported mean respiration rates of 198, 159 and 162 μg C kg^{-1} h^{-1} for D, M and C, respectively, during 35 day incubation measurements at 25°C and 60% water holding capacity. These rates correspond with 56, 58, and 62% of the maximum respiration rates found in this study for D (351 μg C kg^{-1} h^{-1}), M (275 μg C kg^{-1} h^{-1}) and C (262 μg C kg^{-1} h^{-1}), respectively.

5 Conclusions

Gross rate determinations are required to assess processes and to validate mechanistic models. Based on our results, Barometric Process Separation (BaPS) is a suitable method for determining high gross nitrification rates in mineral soils. It can be used for measurements under near-to-field conditions without adding nitrogen or destroying the soil structure, which is essential for filling in the gap in existing knowledge between laboratory studies and field conditions. In future studies the precision of BaPS measurements has to be improved by in situ pH measurements during incubation. This is particularly important for neutral and alkaline agricultural soils.

"Apparent" temperature sensitivity of gross nitrification depends on the local site conditions and therefore more research is necessary to assess different explanations currently under discussion. One possible explanation is microbial adaptation to specific climate conditions. However, substrate availability and substrate quality may also cause different temperature sensitivities. These questions are of special

relevance when effects of future climate change on the soil N cycle shall be predicted by modelling simulations of agricultural soils.

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