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NITRATE UTILIZATION IN A PEAT SOIL UNDER REWETTING CONDITIONS – A RESULT OF A <sup>15</sup>N-NITRATE TRACER APPROACH AT LABORATORY AND FIELD SCALE

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## SUMMARY

The present study was aimed at determining the consumption of nitrate (NO<sub>3</sub><sup>-</sup>) and pathways of NO<sub>3</sub><sup>-</sup> transformation using a [<sup>15</sup>N]NO<sub>3</sub><sup>-</sup>/bromide double-tracer approach. Under field conditions in the rewetted peat sites <sup>15</sup>NO<sub>3</sub><sup>-</sup> consumption occurred rapidly with more than 50 % NO<sub>3</sub><sup>-</sup> consumed within 2 days and 100 % within 8 days after tracer application. Concomitantly <sup>15</sup>N abundances of different soil water N compounds (ammonium, nitrite) increased considerably and lead to the conclusion that, besides commonly known NO<sub>3</sub><sup>-</sup> reduction to nitrite (i.e. denitrification), a reduction of NO<sub>3</sub><sup>-</sup> to ammonium based on added <sup>15</sup>NO<sub>3</sub><sup>-</sup> has simultaneously taken place.

KEY WORDS: denitrification, dissimilatory nitrate reduction, peatlands

## INTRODUKTION

Nitrogen (N) inputs by atmospheric deposition have increased markedly in Europe over the last five decades (e.g. Pitcairn *et al.*, 1995) and may affect sensitive ecosystems that are adapted to nutrient poor conditions such as peatlands (e.g. Bragazza *et al.*, 2004). Recent concerns, however, emphasise a potential risk that an additional input of nitrate (NO<sub>3</sub><sup>-</sup>) by atmospheric deposition may increase denitrification rates and thus, enhance the emission of the greenhouse gas nitrous oxide (Aerts, 1997). Within peat soils NO<sub>3</sub><sup>-</sup> represents a very labile species, since pronounced anaerobic conditions favour a fast microbial consumption of NO<sub>3</sub><sup>-</sup> with denitrification as the major process assumed (Aerts, 1997; Rückauf *et al.*, 2004). However, recent studies suggest that soil NO<sub>3</sub><sup>-</sup> can also be transformed during dissimilatory NO<sub>3</sub><sup>-</sup> reduction to ammonium (NH<sub>4</sub><sup>+</sup>, DNRA) (Rütting *et al.*, 2008; Sgouridis *et al.*, 2009) but only little is known concerning its presence in peatlands (Ambus *et al.*, 1992; Davidsson and Ståhl, 1999; Rückauf *et al.*, 2004).

The present study was aimed at determining  $\text{NO}_3^-$ -N consumption and transformation in a transition bog under drained (water table -30 cm) and rewetted (water table 0 cm) conditions by using a [ $^{15}\text{N}$ ] $\text{NO}_3^-$ /bromide double-tracer approach.

## MATERIAL AND METHODS

### *Study site*

Experiments were performed in the Harz Mountains (central Germany) in a transition bog (670 m a.s.l.) in direct vicinity to the Mt. Brocken (1142 m a.s.l., 51°48'N, 10°37'E). The peat soil was drained in 1750 to 1776 by drainage ditches, then planted with spruces for forestry use and recently partially rewetted by closing the ditches beginning of the year 2005. It extends to an area of 19 ha and is classified as nutrient poor and acidic.

### **Experimental design**

For the laboratory experiments 16 intact soil cores (20 cm diameter, 50 cm height) were cut out of the peat soil at a drained peat site. Field experiments were performed at both drained (FE 1) and rewetted peat sites (FE 2). For the field experiments V2A steel tubes (30 cm diameter, 80 cm height) were pushed 70 cm deep into the peat soil layer (five replicates). Introduced tubes were open at the bottom to permit a natural water table adjustment within the tubes during an experiment. Peat soil columns were then labelled with [ $^{15}\text{N}$ ] $\text{NO}_3^-$ , equivalent to 30 kg N ha<sup>-1</sup> ( $^{15}\text{N}$  abundance of 48 at. %). Concomitantly to  $\text{NO}_3^-$  the conservative tracer  $\text{Br}^-$  was applied to calculate the effective  $\text{NO}_3^-$  consumption in a peat soil column. For soil water sampling miniature suction cups were placed within the tubes in different depths.

### **Chemical and $^{15}\text{N}$ analysis**

Concentration of bromide ( $\text{Br}^-$ ) and  $\text{NO}_3^-$  were performed by ion chromatography (DX 500). The N concentration and  $^{15}\text{N}$  abundance of  $\text{NH}_4^+$ , nitrite ( $\text{NO}_2^-$ ), and  $\text{NO}_3^-$  in soil water samples was analysed by the SPINMAS approach (Russow, 1999; Stange *et al.*, 2007).

### **Calculation of $\text{NO}_3^-$ consumption**

$\text{NO}_3^-$  consumption was calculated based on measured  $\text{Br}^-$  and [ $^{15}\text{N}$ ] $\text{NO}_3^-$  concentrations in peat soil water samples and  $\text{Br}^-$  and  $^{15}\text{NO}_3^-$  amounts applied at the beginning of an experiment. First, dilution (DL) of the  $\text{Br}^-$  tracer was calculated according to Eq. (1).

$$DL = \frac{[\text{Br}^-_{\text{sample}}] - [\text{Br}^-_{\text{zero}}]}{[\text{Br}^-_{\text{applied}}]} \quad (1)$$

$[\text{Br}^-_{\text{sample}}]$  – concentration of  $\text{Br}^-$  in peat soil water sample;  $[\text{Br}^-_{\text{zero}}]$  - concentration of  $\text{Br}^-$  in peat soil water prior to tracer application;  $[\text{Br}^-_{\text{applied}}]$  - concentration of  $\text{Br}^-$  tracer applied.

Afterwards dilution corrected  $^{15}\text{NO}_3^-$  concentration was calculated according to Eq. (2) and then used to calculate  $^{15}\text{Nitrate}$  consumption ( $C_{\text{NO}_3^-}$ ) express in percent according to Eq. (3).

$$[^{15}\text{NO}_3^-_{\text{corr.}}] = \frac{[^{15}\text{NO}_3^-_{\text{sample}}]}{DL} \quad (2)$$

$[^{15}\text{NO}_3^-]_{\text{sample}}$  - concentration of  $^{15}\text{NO}_3^-$  in peat soil water.

$$C_{\text{NO}_3^-} = \frac{([^{15}\text{NO}_3^-]_{\text{corr.}} - [^{15}\text{NO}_3^-]_{\text{applied}})}{[^{15}\text{NO}_3^-]_{\text{applied}}} \cdot 100 \quad (3)$$

$[^{15}\text{NO}_3^-]_{\text{applied}}$  – concentration of  $[^{15}\text{N}]\text{NO}_3^-$  tracer applied.

## RESULTS

### $\text{NO}_3^-$ consumption

At the drained peat sites (FE 1)  $\text{NO}_3^-$  consumption was very low and peaked at only 47 % at the end of FE 1 (Fig. 1). By contrast, at the rewetted field site (FE 2) a more rapid rise of  $\text{NO}_3^-$  consumption was observed, reaching a total consumption of more than 50 % two days and up to 100 % five days after tracer application (Fig. 1).

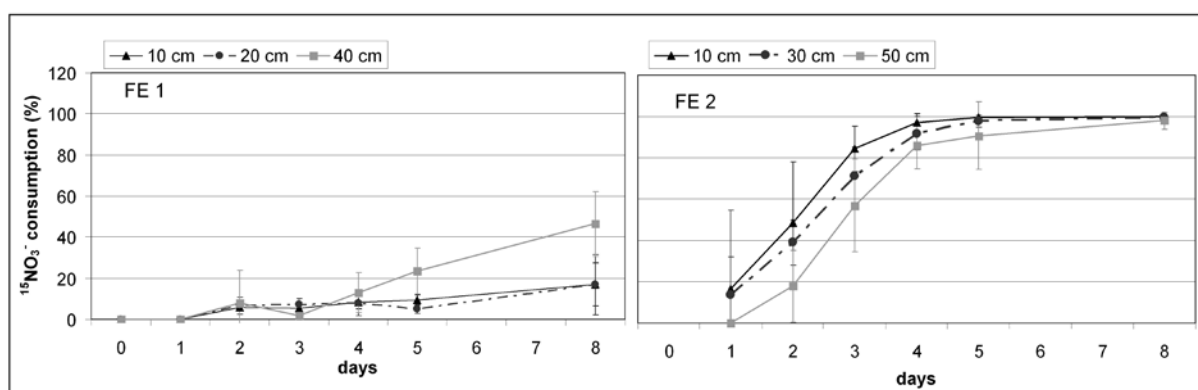


Figure 1. Nitrate ( $\text{NO}_3^-$ ) consumption at the drained (FE 1) and rewetted peat sites (FE 2) (shown as mean and standard deviation). Tracers were applied at day 1.

### $\text{NO}_3^-$ transformation

The  $^{15}\text{NH}_4^+$  concentrations in the peat soil water of the rewetted peat site (FE 2) increased markedly in all considered depths to maximum values of up to  $0.005 \text{ mmol L}^{-1}$  (-10 cm) (data not shown). In the peat soil water of the drained peat site smaller  $^{15}\text{NH}_4^+$  concentrations of maximally  $0.002 \text{ mmol L}^{-1}$  (-10 cm) were observed (data not shown).

At the rewetted peat site (FE 2)  $^{15}\text{NH}_4^+$  abundances increased in all considered depths to a maximal value of 4.2 at. % at the third day of the experiment (Fig. 2a).

Calculated  $\text{NH}_4^+$  formation from  $\text{NO}_3^-$  increased from 3.7 % (-10 cm), 3.3 % (-30 cm) and 3.2 % (-50 cm) at the first day of the experiment to 12 % (-10 cm), 9.2 % (-30 cm) and 7.4 % (-50 cm) at the fourth day of the experiment at the rewetted site (Table 1). At the drained site  $\text{NH}_4^+$  formation from  $\text{NO}_3^-$  was maximally 3.9 % (20 cm) with a very high standard deviation (Table 1).

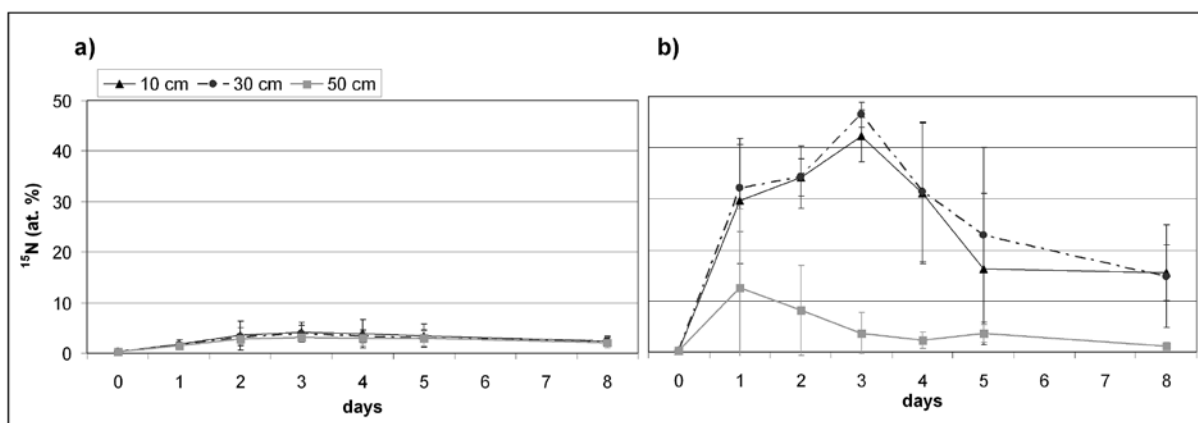


Figure 2. <sup>15</sup>N abundances of a) ammonium (NH<sub>4</sub><sup>+</sup>) and b) nitrite (NO<sub>2</sub><sup>-</sup>) in peat soil water at the rewetted peat site (FE 2) (shown as mean and standard deviation). Tracers were applied at day 1.

Calculated NO<sub>2</sub><sup>-</sup> formation based on NO<sub>3</sub><sup>-</sup> at the rewetted peat site increased from 62.1 % (-10 cm), 67.2 % (-30 cm) and 59.0 % (-50 cm) at the first day of the experiment to maximal values of 90.3 % (-10 cm), 96.1 % (-30 cm) and 97.0 % (-50 cm) reached at the third of the experiment (data not shown). Our study furthermore showed that <sup>15</sup>N abundances of NO<sub>2</sub><sup>-</sup> in the peat soil water at the rewetted peat site (FE 2) significantly increased mainly in the first days of the experiment reaching maximal value of 46 at. % (Fig. 2b).

Table 1: Ammonium (NH<sub>4</sub><sup>+</sup>) formation derived from nitrate (NO<sub>3</sub><sup>-</sup>) at the drained (FE 1) and rewetted (FE 2) peat site (shown as mean and standard deviation). Tracer was applied at day 1.

	NH <sub>4</sub> <sup>+</sup> formation derived from NO <sub>3</sub> <sup>-</sup> (in %)					
	FE 1			FE 2		
Depth	10 cm	20 cm	40 cm	10 cm	30 cm	50 cm
Day 0	0	0	0	0	0	0
1	1.4 ± 0,2	-	0	3.7 ± 3	3.3 ± 1	3.2 ± 1
2	1.6 ± 0,5	1.7 ± 1	2.3 ± 0.4	7.3 ± 7	6.9 ± 2	5.9 ± 2
3	2.3 ± 0,2	2.7 ± 2	-	9.0 ± 6	8.2 ± 3	6.8 ± 3
4	-	-	-	11.8 ± 10	9.2 ± 4	7.4 ± 3
5	-	-	-	n. c.	n. c.	n. c.
8	2.8 ± 1	3.9 ± 5	3.0 ± 1	n. c.	n. c.	n. c.

n.c.: not exactly calculable because of low <sup>15</sup>NO<sub>3</sub><sup>-</sup> abundances, - : not enough sampling water

## DISCUSSION

NO<sub>3</sub><sup>-</sup> consumption rates differed significantly between both peat sites with more than 50 % NO<sub>3</sub><sup>-</sup> consumed within 2 days and 100 % within 8 days after tracer application at the rewetted peat site (see Fig. 1). Reasons for the clear differences between drained and rewetted sites are most likely related to the O<sub>2</sub> availability. At the drained peat site (FE 1) observed redox potentials were significantly higher than observed under water-logged conditions at the rewetted site (data not shown) that have been well in the range reported for microbial NO<sub>3</sub><sup>-</sup> reduction (e.g. denitrification) (Mitsch and Gosselink, 2000). It has been shown in several studies that at

high soil water contents and low O<sub>2</sub> concentration (as often found in peatland soils) NO<sub>3</sub><sup>-</sup> is rapidly utilized (e.g. reduced by denitrifier).

The present study revealed furthermore that under water-logged conditions at the rewetted peat site (FE 2) the <sup>15</sup>N abundance of NH<sub>4</sub><sup>+</sup> increased markedly during the experiment suggesting the microbial process of DNRA (see Fig. 2a, Table 1) whereas under drained conditions the dissimilatory NO<sub>3</sub><sup>-</sup> reduction seems to be less important. The higher O<sub>2</sub> availability observed at the drained peat site is assumed as the reason for the differences between both sites. It was shown in previous studies that DNRA was restricted to strongly reducing conditions. Furthermore NO<sub>3</sub><sup>-</sup> limiting conditions with C:NO<sub>3</sub><sup>-</sup> ratios >12 associated with a shortage of the electron acceptor NO<sub>3</sub><sup>-</sup> seems to favour DNRA over common denitrification (Davidsson and Ståhl, 2000). But whereas the importance of DNRA was clearly pointed out for many ecosystems (particularly for river sediments, riparian zones as well as paddy and forest soils; e.g. Rütting *et al.*, 2008; Sgouridis *et al.*, 2009), there are only a few studies available which consider DNRA in peatland soils (Ambus *et al.*, 1992; Davidsson and Ståhl, 2000). In contrast to our results DNRA was found to be an insignificant process in previous studies (Davidsson and Ståhl, 2000; Rückauf *et al.*, 2004). Besides DNRA we observed increasing <sup>15</sup>N abundances of NO<sub>2</sub><sup>-</sup> at the rewetted peat site to values that were nearly high than the applied NO<sub>3</sub><sup>-</sup> tracer. These results indicate a reduction of the applied NO<sub>3</sub><sup>-</sup> by microbial degradation processes. Denitrification processes are known to be of major importance for the microbial degradation of NO<sub>3</sub><sup>-</sup> favoured by anaerobic conditions in peat soils (Aerts, 1997; Rückauf *et al.*, 2004) and are suggested as the main reason for the observed high NO<sub>3</sub><sup>-</sup> consumption at the rewetted peat sites (see Fig. 1).

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