

# Identification of mechanisms controlling nitrogen export from agricultural lysimeters

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## Zusammenfassung

In der Lysimeterstation Brandis werden seit 1981 Wasser- und Stoffflüsse unter repräsentativer landwirtschaftlicher Nutzung beobachtet. Trotz substantieller Anstrengungen in der Regulierung von Stickstoffüberschüssen in Richtung bedarfsorientierter Düngung zeigen die Sickerwasseranalysen ansteigende oder stagnierende Nitratkonzentrationen in der Grundwasserneubildung auf einer ganzen Bandbreite von Böden. Dieses Paradox wurde mit state-of-the-art Methoden untersucht um herauszufinden aus welcher Quelle das Nitrat im Sickerwasser hauptsächlich stammt. Analysen von Boden- und Sickerwasserproben, in Kombination mit historischen Tracerexperimenten, zeigen deutlich den dominierenden Einfluss der bodenorganischen Substanz auf den Stickstoffhaushalt, dessen Dynamiken und die Nitratkonzentrationen des Sickerwassers. Die Ergebnisse können somit erklären warum die Regulierungsbemühungen bisher nicht zu den gewünschten Reduktionen in den Nitratkonzentrationen der Sickerwasserflüsse geführt haben.

Schlagwörter: Stabilisotope, <sup>15</sup>N, <sup>18</sup>O, Nitrat, Sickerwasser

## Summary

The lysimeter station Brandis provides observations of water and solute fluxes under representative agricultural landuse since 1981. Despite substantial efforts and success in regulation and assessment of fertilizer needs and the reduction of fertilization excess, the seepage water analysis reveals increasing or stagnating levels of nitrate concentration in groundwater recharge in a broad range of soil types. We investigated this paradox with current state-of-the-art methods to identify the relevant nitrogen sources of the seepage water. Analysis of current soil and seepage water samples, in combination with historic tracer experiments, highlight the substantial role of the soil organic nitrogen pool on nitrogen dynamics and recharge concentrations in all relevant soils. Thus, the results hold an explanation why the current regulation efforts have not yet led to the desired reductions in nitrogen loadings of seepage water fluxes.

Keywords: Stabilisotope, <sup>15</sup>N, <sup>18</sup>O, Nitrat, Sickerwasser

## Introduction

The lysimeter station Brandis provides observations of water and solute fluxes under representative agricultural landuse since November 1980. Since the beginning of the lysimeter studies seepage water analyses showed high levels of nitrate concentration in groundwater recharge in a broad range of the investigated soil types. Despite substantial efforts in regulation of fertilizer applications since the 90s and some success in the reduction of fertilization excess, no significant change in seepage water nitrate concentrations is observed yet. Furthermore, the long-term N-balances show that only a fraction of the fertilizer excess nitrogen is exported with the seepage water. To gain

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a better understanding of the reasons for these observations the following questions are important:

- Does excess fertilizer leach through the root zone after the vegetation period and is exported with the seepage water?
- Which part of the soil N-cycle contributes to the seepage water nitrate export?
- Can residence times of mineral fertilizers be estimated?
- Which processes control the nitrogen export in agricultural soils?

Three potential sources for nitrate in seepage water are relevant in agricultural systems: (1) nitrogen from atmospheric deposition, (2) nitrogen from fertilization and (3) nitrogen from soil-microbial processes such as nitrification of soil organic matter. Nitrate consists of two elements, nitrogen (N) and oxygen (O), which both have stable isotopes. Nitrogen is mostly  $^{14}\text{N}$  (~99.6%), nitrogen containing an additional neutron is referred to as  $^{15}\text{N}$  (0.3%). Similar ratios are observed for the very common oxygen isotope  $^{16}\text{O}$  (99.7%) and the heavier  $^{18}\text{O}$  (0.2%). Isotope ratios for oxygen ( $^{18}\text{O}/^{16}\text{O}$ ) and nitrogen ( $^{15}\text{N}/^{14}\text{N}$ ) are usually reported as  $\delta$ -values (‰), which is the isotope ratio of the analyzed substance relative to a standard of known composition (Kendall & Caldwell 1998). The common reference for nitrogen is air and the reference for oxygen is Vienna mean standard ocean water (VSMOW).

Fortunately, the three main sources for nitrate differ significantly in terms of their isotope ratios, in the following referred to as  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  (delta-Notation). The differences between the potential nitrogen sources are shown for both isotope ratios in *Figure 1*. While all three sources overlap significantly in their  $\delta^{15}\text{N}$ -values, they can clearly be discriminated by their  $\delta^{18}\text{O}$ -values. Consequently, assessing the isotope ratios of nitrate contained in the seepage water is a powerful tool to identify its sources and shed some light on the controlling processes (Clark & Fritz 1997, Xue et al. 2009).

Aim of this study is to analyze the isotope signatures of the various potential sources of the seepage water nitrate in selected lysimeters in Brandis in order to shed some light on the potential origin of the seepage water nitrate and gain a better understanding of the underlying mechanisms controlling the nitrogen storage and nitrate export from those soils. Furthermore, we want to assess if and in which way the seepage-water nitrate in lysimeter is related to agricultural management practices and fertilization strategies.

## Material and Methods

### Soil

The following analysis will focus on a single lysimeter, although the analysis have been performed on eight lysimeters from eight different soil types. A short description and

Figure 1: Ranges of typical nitrate sources in agricultural systems. Modified from Kendall (1998), with data from Xue et al. (2009). The lower three boxes further differentiate the basic substrate from which the nitrogen is produced by soil microbial processes, such as nitrification.

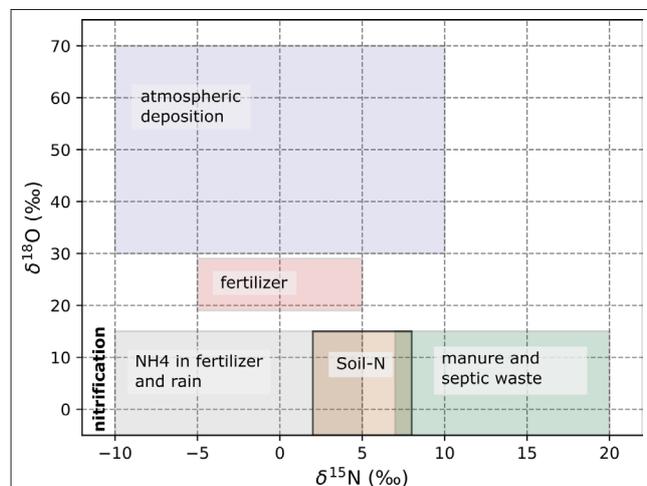


Table 1. Soil description of the investigated lysimeters along with observed values for the field capacity (FC), the maximum field capacity ( $FC_{max}$ ), the average annual seepage water amount ( $SW_{RP}$ ) in the reference period 1981 – 2010 and in the last Decade ( $SW_{LD}$ ). Also the displacement risk (DR) and the average nitrogen concentration  $C_{LD}(NO_3)$  in the last decade as well as the average nitrogen excess ( $NE_{LD}$ ) are given, the latter includes the atmospheric deposition.

Lysimeter	Soil description	FC ( $FC_{max}$ ) (mm/a)	$SW_{RP}$ (mm/a)	$SW_{LD}$ (mm/a)	DR (-)	$C_{LD}(NO_3)$ (mg/l)	$NE_{LD}^*$ (kg/ha)
1/7	Lessivated stagnic Cambisol	114 (180)	96	134,4	low	126	38

\* includes measured atmospheric BULK-deposition

some of the most important hydrological properties as well as some information for nitrogen export are given in *Table 1*. Lysimeter 1/7 contains a soil with an average effective field capacity of 114mm, with observed maxima around 180mm for crops with deep root systems. Within the last decade, the average annual seepage water volume was 134 mm and the average nitrate concentration was 126mg/l. The average annual nitrogen excess, the difference between input at the surface and nitrogen withdrawn with the harvest, was 38kg/ha.

### Long-term Management

A brief overview about the long-term nitrogen balance with its components is given in *Table 2*. Three distinct changes occurred in the agricultural management in the past 40 years. In the first period from 1980 to 1992, nitrogen supply was based on a mixture of mineral and organic fertilizers. From 1993 to 1998 a period of ecological farming followed, fertilization was based on legumes and a single application of organic fertilizer and the overall nitrogen balance was negative. Intensive agricultural management was reestablished in 1999, the fertilization was mainly based on mineral fertilizers and fertilization was conducted according to the respective guidelines and regulations. The decadal nitrogen excess ( $N_E$ ) in *Table 2* clearly shows, that increasing regulation efforts led to a reduction of the fertilization excess on this lysimeter, unfortunately this is not the case for all lysimeters. However, the table also shows that the nitrogen export with the seepage water ( $N_{SW}$ ) over this long period is only a fraction of the nitrogen excess. In the past 40 years, only 45% of the nitrogen fertilization excess was lost with the seepage water. The nitrogen balance, which is the difference of  $N_E$  and  $N_{SW}$  indicates an accumulation of 1.4 t-N/ha in the soil over the past 40 years.

### Sampling scheme

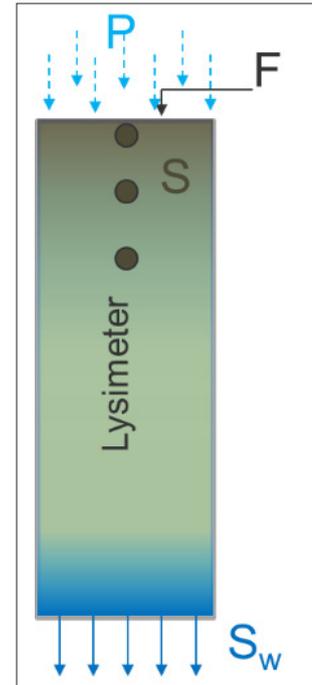
As noted earlier, detailed knowledge about the isotope ratios of the potential nitrogen sources is necessary to be able to relate the nitrate in the seepage water to one, or a mixture of these sources. To verify the literature sources for the atmospheric deposition and the fertilizers on one hand and to gain a more detailed insight on the  $^{15}N$

	$N_{Fer}$ (kg/ha)	$N_E^*$ (kg/ha)	$N_{SW}$ (kg/ha)	$N_{SW}/N_E$ (%)	$N_B = N_E - N_{SW}$ (kg/ha)
1980 - 1989	2377	1627	279	17	1384
1990 – 1999 <sup>A</sup>	670	151	113	75	38
2000 – 2009	1391	501	395	79	106
2010 – 2019	1493	381	429	112	-48
<b>1980 – 2019</b>	<b>5931</b>	<b>2660</b>	<b>1216</b>	<b>46</b>	<b>1444</b>

<sup>A</sup> decade contains a period of ecological farming from 1993 – 1998; \* includes measured atmospheric deposition

Table 2. Overview about the N-fertilization ( $N_{Fer}$ ), the nitrogen excess ( $N_E^*$ ), the nitrogen exported with the seepage water ( $N_{SW}$ ), the ratio of the excess and the seepage water loss and the nitrogen balance ( $N_B$ ) for the past 4 decades.

Figure 2. Sampling scheme for the isotope analyses, consisting of precipitation samples (P), samples of the fertilizer (F), and 4 different seepage water samples ( $S_w$ ) per year. To gain a better insight about the  $^{15}\text{N}$  background in the soil organic and potential depth profiles, three soil probes (S) were taken per lysimeter for analysis.



distribution within the soils on the other hand the sampling scheme given in *Figure 2* was applied. Precipitation samples were collected with BULK collectors and combined to monthly samples. Fertilizers applied in 2019 and 2020 were analyzed as well as soil samples from the upper three soil horizons, taken in autumn of 2019. Most importantly, four monthly seepage water samples for each seepage water period in 2019 and 2020 were analyzed for the isotope ratios of the contained nitrate. Seepage water samples were selected to include: (1) the beginning of the seepage water period, (2) two months with the highest seepage water amounts and (3) a sample in the recession of the seepage water occurrence.

### Isotope analysis

All water samples were filtered by a  $0,2\mu\text{m}$  screen before filling in 50ml polyethylene containers and stored frozen until analysis. A modified denitrifier method developed by Stock et al. (2020) was applied for sample preparation (transformation of  $\text{d}^{18}\text{O}$  and  $^{15}\text{N}$  from  $\text{NO}_3$  to gaseous  $\text{N}_2\text{O}$ ) before the isotope analysis of the samples. The simultaneous analysis of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  was conducted by a stable isotope mass spectrometer MAT253 with Gas-bench II and a denitrification kit (all Thermo-Fisher Scientific). The solid samples (soils and fertilizer), were grinded after freeze-drying and burned to  $\text{N}_2$  in an elemental analyzer (EA 3000, Eurovector). The resulting gas was analyzed in the MAT253 stable isotope mass spectrometer. Calibration was achieved with the IAEA isotope standard  $\text{NO}_3$  (+4.7‰  $\text{d}^{15}\text{N}$ , +25.6‰  $\text{d}^{18}\text{O}$ ), USGS34 (-1.8‰  $\text{d}^{15}\text{N}$ , -27.9‰  $\text{d}^{18}\text{O}$ ) und USGS32 (+180‰  $\text{d}^{15}\text{N}$ , +25.7‰  $\text{d}^{18}\text{O}$ ).

## Results

### Atmospheric Deposition

The nitrate contained in five selected bulk precipitation samples collected between 2019 and 2020 have been analyzed and showed expected variations in  $\delta^{15}\text{N}$ -values between -3.3‰ and 15‰. Contrastingly, measured  $\delta^{18}\text{O}$ -values showed a larger variation between 57.7‰ and 83.1

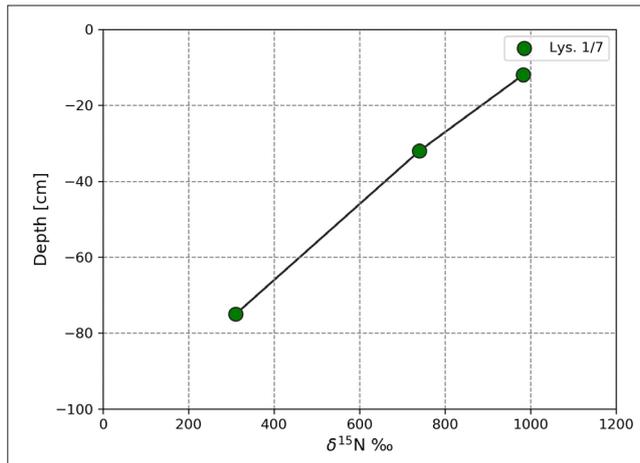


Figure 3. Depth profiles of the  $\delta^{15}\text{N}$  values for lysimeter 1/7. Note that the high  $\delta^{15}\text{N}$  values for lysimeter 1/7 are due to the application of artificially  $^{15}\text{N}$  enriched fertilizers in the past.

## Fertilizer

Lysimeter 1/7 received a classical sulfur enriched mineral nitrogen fertilizer (InnoFert Star). The fertilizer has a  $\delta^{15}\text{N}$  ratio close to zero, which is expected as air is used as nitrogen source during production. The  $\delta^{18}\text{O}$ -value of 25.4‰ also fits into the expected range for mineral fertilizers.

## Soil Profile

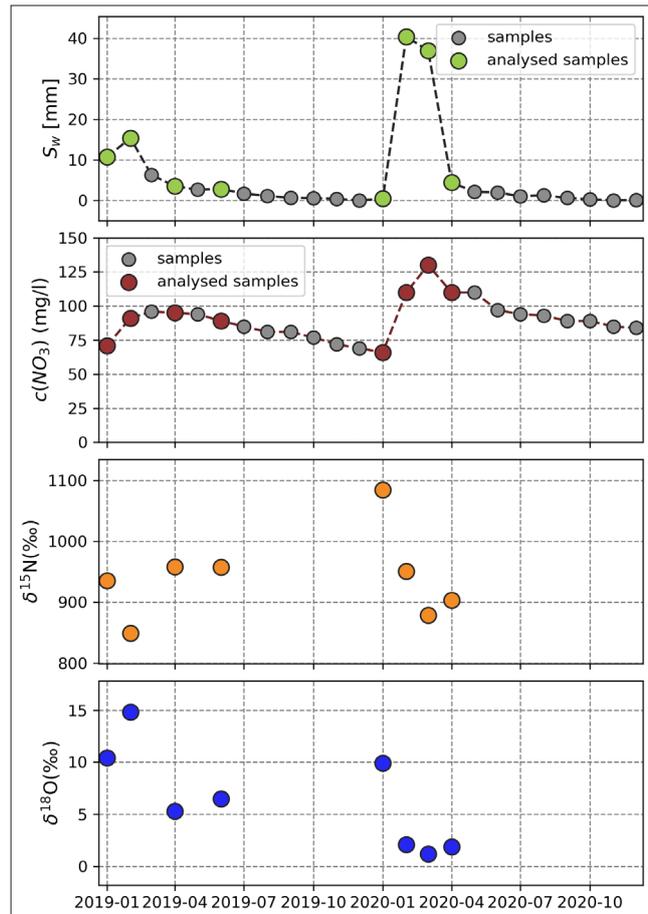
The nitrogen contained in the soil of lysimeter 1/7 has unusually high  $\delta^{15}\text{N}$  values in all three depths, as is shown in *Figure 3*. This profile is explained by the application of artificially enriched  $^{15}\text{N}$  fertilizer as tracer in the 1970s and 1980s. Although the documentation of these experiments is incomplete, it is known that lysimeter 1/7 was fertilized at least 8 times with  $^{15}\text{N}$  enriched fertilizer. The experiments were initiated to estimate the N-use efficiency of different crops. However, significant parts of the fertilizer were incorporated into the soil organic N-pool (Russow et al. 1996) and caused substantial enrichments. Although only a fraction of the historic enrichment is still measurable, it causes a clearly labeled soil organic N-pool. Lysimeter 1/7 exhibits the highest  $\delta^{15}\text{N}$  values ( $\delta^{15}\text{N} \sim 970\text{‰}$ ) close to the surface in the soil layer with the highest N-content. The  $\delta^{15}\text{N}$ -values decrease with increasing soil depth and decreasing total N-content of the soil. Absolute values for  $\delta^{15}\text{N}$  in the second and third soil layer are 740‰ and 310‰, respectively.

## Seepage water nitrate

Monthly seepage water volumes observed for both years on lysimeter 1/7 are shown in *Figure 4*. The seepage water period 2019 was rather short and driven by the heavy drought of 2018 resulting in seepage water volumes well below average. The following vegetation period of 2019 can also be characterized as dry with low precipitation volumes and high evapotranspiration demand. Average precipitation amounts in autumn of 2019 caused a slow refill of the soil water deficit, but the first seepage water was observed in January 2020. A very wet February caused above average seepage water flows, which were able to compensate the late beginning (compared to the average of 1981-2010) of the seepage water period.

Nitrate concentrations in the seepage water of lysimeter 1/7 exceed the drinking water threshold in all months during the isotope measurement campaign. Concentrations increase with the beginning, and tend to decrease with the recession of the seepage water period and varied between 66mg/l and 130mg/l. Eight monthly seepage water samples have been selected for the isotope analysis. The resulting  $\delta^{15}\text{N}$ -values varied between 849‰ and 1085‰, which shows that the seepage water nitrate is heavily enriched in  $^{15}\text{N}$  in all samples. The observed  $\delta^{18}\text{O}$ -values lie between 1.2‰ and 14.8‰.

Figure 4: Time series of the monthly seepage water volumes (top), nitrate concentration (middle-top) the  $\delta^{15}\text{N}$ -values of the seepage water nitrate (middle-bottom) and its  $\delta^{18}\text{O}$ -values (bottom) of Lysimeter 1/7.



To allow an easier source attribution of the nitrate transported in the seepage water, the data is shown in a dual isotope plot (after Kendall 1998) in Figure 5. According to the very high  $\delta^{15}\text{N}$ -values in all seepage water samples, nitrification from soil organic matter seems to be the major nitrate source. This hypothesis is further supported by the  $\delta^{18}\text{O}$ -values, which are also in the typical range for nitrate from soil organic-N (Kendall, 1998). It should also be noted, that no simple relationship between  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ -values and nitrate concentration is observed. Having the advantage of a soil organic nitrogen pool heavily enriched in  $^{15}\text{N}$  with a distinct  $\delta^{15}\text{N}$ -profile, the  $\delta^{15}\text{N}$ -values might give an indication of the soil depth in which the nitrate was derived by nitrification. Following this hypothesis, the nitrate in most of the samples was derived within the first 30cm of the soil. Following the common assumption that nitrate produced by nitrification contains two oxygen atoms from soil water and one from soil  $\text{O}_2$  (Hollocher 1984), variations in  $\delta^{18}\text{O}$  values of the sample would then mainly depend on moisture state and if evaporation or transpiration dominated the soil water reduction process (Hsieh et al. 1998). Water reduction by transpiration causes an enrichment of  $\delta^{18}\text{O}$  in the remaining soil water, thus it could further be speculated that some samples contain nitrate from nitrification in the upper soil horizons under rather dry conditions. Especially the samples from 01/2019, 02/2019 and 01/2020 show high  $\delta^{18}\text{O}$ -values ( $\delta^{18}\text{O} > 10\text{‰}$ ) and the massively enriched  $\delta^{15}\text{N}$ -values of the soil organic matter pool.

## Summary and Discussion

Isotope analysis of the nitrate contained in the seepage water of lysimeters under agricultural land use were initiated to gain a better understanding of the nitrogen dynamics and identify the relevant nitrogen sources. This contribution presented detailed

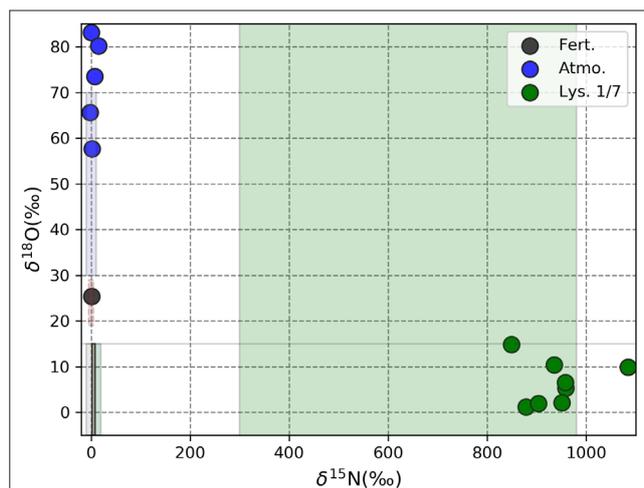


Figure 5. Dual isotope ratio plot for the monthly seepage water nitrate samples of lysimeter 1/7, the fertilizer sample and the nitrate in the atmospheric deposition. Boxes on the left show the most likely ranges of nitrate from different sources (deposition, fertilizer, soil), the green box covering the range  $310‰ < \delta^{15}\text{N} < 970‰$  is the range of values observed in the soil profile.

information on the results of these analyses for one specific lysimeter. The results clearly show, that the nitrate contained in the seepage water of the last two years, originates with very high probability from the soil organic N-pool. No indications for a direct percolation of fertilizer nitrogen are found in the data. The soil profile analysis revealed a highly in  $^{15}\text{N}$  enriched soil nitrogen pool, which was caused by applications of artificially enriched fertilizers as tracers in the 1970s and 1980s. The results further indicate that not only the source can be identified, but potentially also space and time of the nitrification process. If this holds to be true must be examined with more detailed analyses and ongoing measurement campaigns.

The findings from the long-term observations of the nitrogen balances and the isotope analyses lead to some important conclusions, which need to be considered when utilizing lysimeters for investigations in nitrogen dynamics in agricultural settings:

- The soil organic N-pool is an important buffer and driver of the nitrogen dynamics and distribution in soils.
- The nitrogen export by seepage water nitrate might not directly depend on the agricultural nitrogen balance, but rather on the conditions for nitrification after harvest.
- Nitrogen residence times in the lysimeters might be longer than water residence times.

Based on the results, we strongly recommend considering isotope analyses as a valuable tool for lysimeter-based investigations into nitrogen dynamics. They can reveal the relationship between agricultural management and nitrate based nitrogen loss with the seepage water, which appears in our case to be more complex than a simple displacement of fertilizer excess.

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