Effect of long-term nitrogenous losses to the ^{15}N natural abundance

M. Kriszan ,W. Kühbauch, W. Amelung, J. Schellberg und T. Gebbing

Department of Crop Science and Resource Conservation, University Bonn

Introduction

High amendments of nitrogenous fertilizers stimulate biomass production and increase the N content in plant material. However, any N fertilization is accompanied by undesirable side effects related to N losses through ammonia volatilization, NO_3^- leaching or nitrogenous trace gas emissions (DITTERT ET AL., 1998). The N transformations in any ecosystem lead to N isotope fractionation, i.e. discrimination occurs against the heavier ^{15}N form. Such $\delta^{15}N$ fractionations range from 0‰ to 35‰ for N_2 fixation and NH_3 volatilization, respectively (HÖGBERG, 1997). According to the Rayleigh model (ROBINSON, 2001) all products that are emitted to the environment (NH_3, N_2O, NO, N_2, NO_3^-) are generally ^{15}N depleted, and, hence, the remaining natural N-sources are enriched in ^{15}N (HÖGBERG, 1997). Such enrichment might be a promising signature to reconstruct N losses due to management in different compartments of an agricultural farm (WATZKA ET AL., 2006).

The aim of the present study was to report on the variety of $\delta^{15}N$ values and total N stocks in a grassland farm. We hypothesized that different forms of N fertilization can be traced back by characteristic $\delta^{15}N$ values in soils and plants. Furthermore, we hypothesized that elevated $\delta^{15}N$ values of various N-pools indicate an N-surplus emitted to the environment. We explored whether the $\delta^{15}N$ values of harvested plant biomass is secondarily influenced by floristic composition, due to plant specific isotope discrimination processes.

Materials and Methods

To relate N losses to fertilizer N, samples were collected from a 22 year old field lysimeter experiment that has been conducted at the Research Station Rengen (Eifel Mountains, Germany). The experiment was performed in three different treatments in randomised complete block design, with 3 blocks consisting of 5 permanent grassland plots (2 x 6 m). N was (Tab.1) either applied in organic fertilizer (cattle slurry), mineral fertilizer (calcium ammonium nitrate) or as a mixture of both (Tab. 1). Four cuts per season were performed.

Tab. 1: Experimental design of fertilizer treatments

Type I	unfertilized control
Type II	240 kg org N
Type III	480 kg org N
Type IV	200 kg min N
Type V	200 kg min N + 160 kg org N

Bulk soil samples were taken from each plot concurrently and were then divided into subsamples from 0-5 cm, 5-10 cm and 10-30 cm soil depth. Total N content as well as natural ^{15}N abundances in all samples were determined by dry combustion using an elemental analyzer (NA 1108, Carlo Erba, Milan, Italy) coupled with a continuous-flow isotope ratio mass spectrometer (Delta Plus, ThermoFinnigan, Bremen, Germany).

All laboratory N and $\delta^{15}N$ measurements were carried out at the Department of Grassland Science at TUM, Weihenstephan.

Results and Discussion

With increased N fertilization the total N contents of soils did not hardly changed (data not shown), suggesting that N losses in soils increased as a result of increased fertilizer application. Indeed the $\delta^{15}N$ values of both soils and harvested plant biomass increased with the amount of applied N fertilizer (Fig. 1 and 2). Soil $\delta^{15}N$ values ranged from 1,8 ± 0,2‰ to 6 ± 0,2‰ in upper horizons and 3,5 ± 0,5‰ to 5,5 ± 0,6‰ in deeper soil layers. The results support the hypothesis, that increasing N applications were reflected by increased soil $\delta^{15}N$ values.

At present we only have the $\delta^{15}N$ value for the mineral fertilizer, which averaged -1 ± 0,2‰. Thus, the increased addition of the $\delta^{15}N$ value with increased inorganic fertilization is not due to the fertilizer signal itself – it must be due to N isotope fractionation which discriminates against the heavier ^{15}N (DAWSON, 2002, HANDLEY and RAVEN, 1992 YONEYAMA, 1996) when N losses increase (HÖGBERG, 1997). Processes leading to N losses result in considerable fractionations, especially during NH_3 volatilization (29‰), denitrification (0-33‰) and nitrification (15-35‰). Accordingly, products of N fractions lost to the environment (NH_3, N_2O, NO, N_2, NO_3^-) are ^{15}N depleted while the residual N-sources are enriched in ^{15}N (HANDLEY and RAVEN, 1992, YONEYAMA, 1996).

Plots receiving organic fertilizer compared to mineral fertilizer showed higher $\delta^{15}N$ values in each soil depth (Fig. 1), primarily due to microbial processes and ammonia volatilization processes during storage (CHOI, 2003). Moreover, differences in soil and plant $\delta^{15}N$ could be caused by high amounts of N lost to the atmosphere during slurry application (YONEYAMA, 1996).

Similarly to soils, plant $\delta^{15}N$ increased with increasing amount of applied N, depending on the N form applied. The above ground total biomass $\delta^{15}N$ values ranged from -1,2 ± 0,5‰ to 4,4 ± 0,3‰ (Fig. 2). This finding suggests that major N signals from the fertilizer N were recovered in the plants, as expected. Plant $\delta^{15}N$ values were correlated with the corresponding top soils (Fig. 3) for 4 out of 6 plant species (Fig. 3). Exceptions were the $\delta^{15}N$ signals of *T. repens* L. and *T. pratense* L. (-0,8 ± 0,3‰ to -0,3 ± 0,1‰.), which did less clearly follow the $\delta^{15}N$ signals of the surface soils (Fig 3). Differences between isotope signatures of sources and sinks could be explained furthermore by enzyme-mediated reaction discriminating against ^{15}N (HANDLEY and RAVEN, 1992).

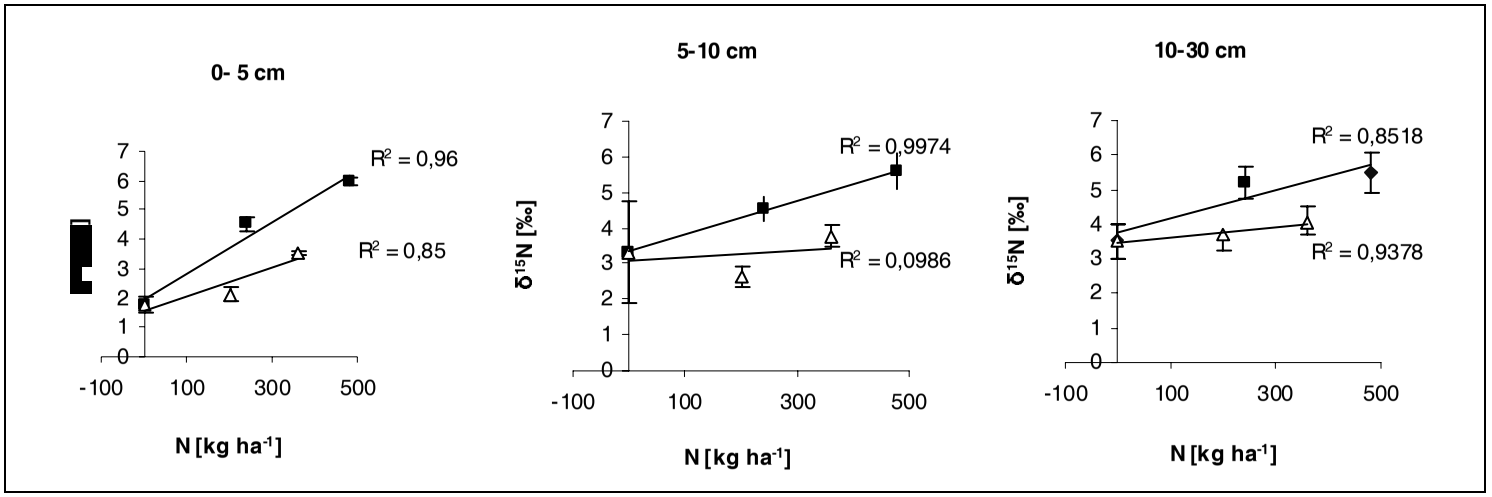

Fig. 1: $\delta^{15}N$ abundances of soils in relation to amount of N applied as organic fertilizer (closed symbols) and mineral/ mixed fertilizers (open symbols) in different soil depths

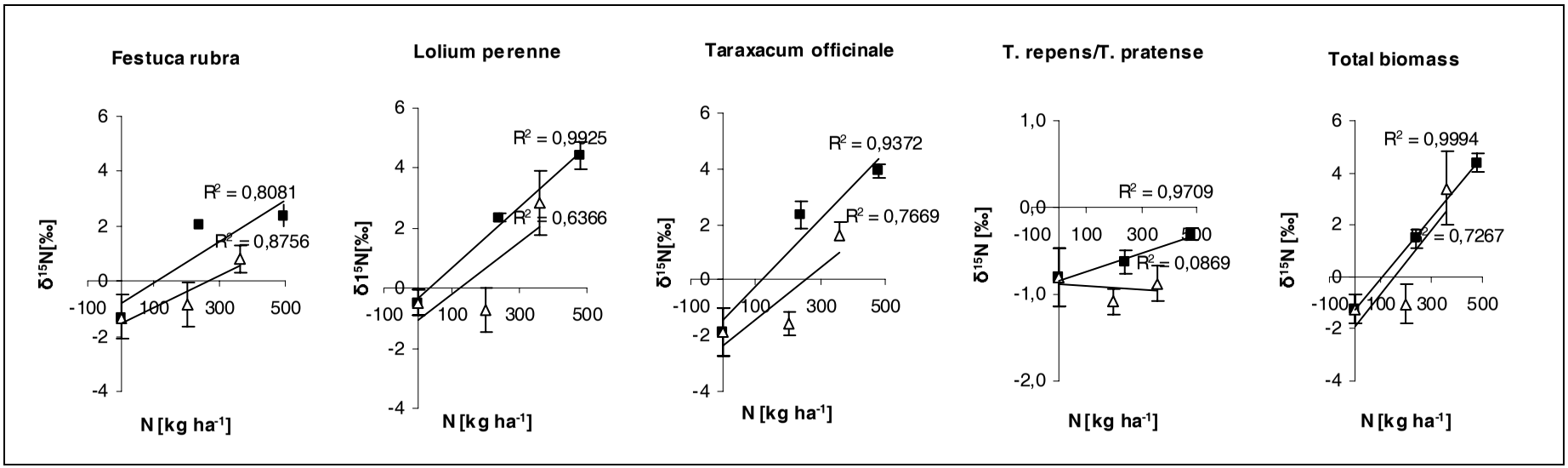

Fig. 2: $\delta^{15}N$ abundances of harvested plant material in relation to the amount of N applied (for symbols see Fig.1)

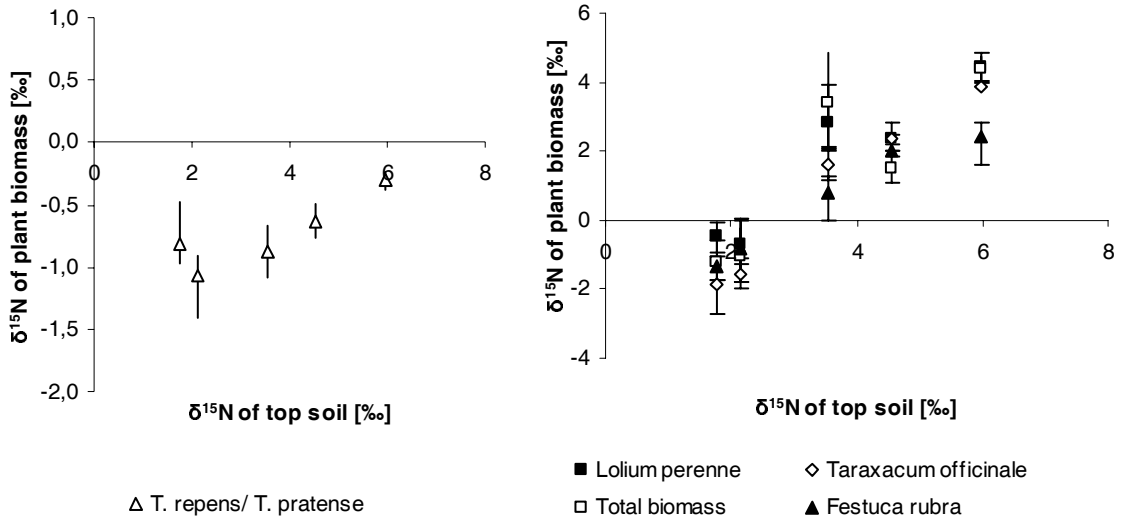

Fig. 3: Relation between $\delta^{15}N$ of top soils and $\delta^{15}N$ of plant biomass

Especially mineral N that is taken up by plants is potentially depleted in heavier N isotopes because of discrimination processes when liberated from organic pools by mineralization (KERLEY and JARVIS, 1996). Even microbial heterothrophs produce ^{15}N depleted excreta, which are available for N uptake by plants (NADELHOFFER et al., 1996).

Distinctions in $\delta^{15}N$ among plant species may reflect differences in plant growth, resource acquisition strategies or varieties in $\delta^{15}N$ of soil N pools for which they compete (NADELHOFFER et al. 1996).

The $\delta^{15}N$ values of soils and above ground biomass were highly correlated with the fertilizer management. Thereby not only the quantity but also the chemical form of applied N- fertilizer was reflected by the variations in ^{15}N abundance of each component. Despite the large variability of $\delta^{15}N$ values found in different compartments of the ecosystems, our results thus clearly showed that it is possible to use the $\delta^{15}N$ natural abundance technique to track hot spots of inefficient N usage in a 22 year old experiment.

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