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Martin H. Gerzabek, Holger Kirchmann, Georg Haberhauer, Friedrich Pichlmayer. The response of soil nitrogen and 15N natural abundance to different amendments in a long-term experiment at Ultuna, Sweden. Agronomie, 1999, 19 (6), pp.457-466. hal-00885944

### HAL Id: hal-00885944 https://hal.science/hal-00885944

Submitted on 11 May 2020  $\,$ 

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## The response of soil nitrogen and <sup>15</sup>N natural abundance to different amendments in a long-term experiment at Ultuna, Sweden

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(Received 10 November 1998; accepted 20 May 1999)

**Abstract** – In a long-term field experiment on a clay loam soil at Uppsala, Sweden, changes in nitrogen contents, natural abundance of <sup>15</sup>N in the topsoils receiving various organic amendments at the rate of 2 000 kg C ha<sup>-1</sup>year<sup>-1</sup> and different rates of nitrogen mineralisation were studied. Cropping resulted in clearly lower N losses from the topsoil (0–20 cm) compared to the bare fallow plots. Green manure, animal manure and sewage sludge increased the N<sub>1</sub> inventory significantly; for the latter two treatments an equilibrium of N input and N output was not reached within 35 years of application. The highest N efficiency with respect to plant uptake and the highest N losses were recorded for the mineral N-treated plots. <sup>15</sup>N abundances were clearly affected by N input, differing in isotopic signature introduced through the amendments. This effect was used to derive the relative input of 'stable' N from green manure and peat in comparison with the difference method. (© Inra/Elsevier, Paris.)

fertiliser / isotopic abundance / long-term experiment / nitrogen / manure

**Résumé – Réponse de l'azote du sol et de l'abondance naturelle de** <sup>15</sup>N à différents amendements organiques dans une expérience à long terme à Ultuna, Suède. Une expérience à long terme a été conduite sur un sol limonoargileux à Uppsala, Suède. Les modifications de la teneur en azote et de l'abondance naturelle de <sup>15</sup>N dans la couche superficielle ont été étudiées en fonction des apports de différents amendements organiques correspondant à 2 000 kg C ha<sup>-1</sup>·an<sup>-1</sup> avec différents taux de minéralisation de l'azote. Sous culture il apparaît clairement une plus faible perte en azote de la couche superficielle comparativement à un sol nu non cultivé. Les apports d'engrais vert, de fumier et de boues de station d'épuration ont accru significativement la teneur totale en azote Nt et pour les deux premiers traitements l'équilibre entre les apports et les pertes d'azote n'a pas été atteint au cours de 35 ans d'application. La meilleure efficience de l'azote en ce qui concerne l'extraction par la plante et la perte la plus élevée furent enregistrées pour les parcelles qui recevaient un apport d'azote minéral. L'abondance de <sup>15</sup>N a été clairement affectée par les types d'apport

Communicated by Marco Trevisan (Piacenza, Italy)

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d'amendements dont les signatures isotopiques étaient différentes. Cette particularité a été utilisée pour déduire l'apport relatif d'azote « stable » à partir d'un engrais vert et de la tourbe comparativement à la méthode différentielle. (© Inra/Elsevier, Paris.)

amendement / abondance isotopique / expérience à long terme / azote / fumure organique

### 1. Introduction

Nitrogen is one of the most important plant nutrients. The major sources of N supply to plants are i) the mineralisation of soil nitrogen, ii) the application of mineral or organic fertilisers, iii) the wet and dry deposition of N compounds, and iv) the release of nitrogen from residues of N fixing plants. The mineralisation of soil nitrogen is influenced by the same factors which govern soil organic matter build-up and turnover. Thus, climate, soil texture, application of fertilisers and manures [16] and different management practices [2] are important factors in this respect. Quantification of N release from manures and the soil N pool remains difficult, although isotopic methods offer some interesting options [3]. Another question, which is today considered to be of high relevance, concerns the losses of nitrogen from fertiliser and manure. These losses can affect both the groundwater by increasing the nitrate concentration and the atmosphere by the release of greenhouse gases [20].

Short-term studies on SOM turnover and buildup are not feasible owing to the high variability introduced by environmental factors. Quantification of input and output needs longer observation periods; long-term experiments, therefore, seem to be ideal for evaluating effects of agricultural practice on soil carbon and nutrients [15].

The natural abundance of <sup>15</sup>N in soil can be altered by several factors. Besides changes due to microbial activity in soil [3], differences in the vegetation cover and tillage [19] and the long-term application of N fertilisers and organic manures can influence <sup>15</sup>N abundances. The latter effect may be used to quantify the stable portion of nitrogen after a certain time period of continuous manure application [21].

The Ultuna organic matter experiment, started in 1956, was designed to study soil organic matter and structural changes in soils under a range of manurial treatments and inorganic fertilisers. The same amount of carbon (on average 2 000 kg C ha<sup>-1</sup> year<sup>-1</sup>) has been applied through a range of organic amendments. The experiment, therefore, enables us to compare changes in both amount and composition of soil humus as a result of application of different organic manures. In previous publications the impact of organic manures on soil aggregate stability [4], the sulphur balance [11] and on soil organic matter including humification [5] were reported. In this paper, changes in the nitrogen contents of topsoils due to long-term application of different manures and their effect on the natural abundance of <sup>15</sup>N are described. Nitrogen contents in the topsoil are explained by a nitrogen balance. Half-lives of fertiliser N derived from the difference method are compared with the results of the isotopic method.

### 2. Materials and methods

### 2.1. Site and treatments

The field experiment is located in central Sweden, Uppsala, on a Eutric Cambisol (FAO) with 37% clay and 41% silt. The parent material consists of postglacial clay with illite as the main clay mineral. A complete documentation of the experiment and compilation of data can be found in Kirchmann et al. [10]. In 1956 the soil (0–20 cm deep) had 15 g kg<sup>-1</sup> of organic carbon, 1.7 g kg<sup>-1</sup> of nitrogen and a pH of 6.6. The experimental design consists of 14 treatments, laid out in duplicate in a randomised block design. The individual plots (2 m × 2 m), were separated by pressure-treated wooden frames. Five of the treatments, fallow, no-N, green manure, animal manure (well decomposed) and peat (sphagnum) were selected for intensive measurements

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in this study. Additional treatments (sewage sludge,  $Ca(NO_3)_2$  and  $(NH_4)_2SO_4$ ) were evaluated only in 1991. The application of organic amendments, analysed before use, was based on equal amounts of ash-free organic matter amounting to 2 000 kg C ha<sup>-1</sup> year <sup>-1</sup> on average. Organic matter was added in 1956, 1960, 1963 and thereafter every second year by hand. All plots received a dressing of 20 kg P ha<sup>-1</sup> in the form of superphosphate and 35-38 kg K ha<sup>-1</sup> in the form of potassium chloride annually in spring. Cereals (70 %), rape crops (25 %) and fodder beet (5 %) were grown alternately. No N-fixing plants were included in the crop rotation. At harvest the above-ground portion of the crop was completely removed. Topsoil samples (0-20 cm) were taken in autumn before the organic matter was added. They were air-dried, passed through a 2-mm sieve and then stored.

#### 2.2. Analysis

Total nitrogen, organic carbon and  $\delta^{15}N$  were measured in soil samples (1956, 1967, 1975, 1977, 1979, 1981, 1983, 1985, 1987, 1989, 1991, 1993, 1994), and in the green manure, animal manure, peat (1975, 1979) and spring wheat or rye (1987, 1989, 1991) using an elemental analyser coupled to a mass spectrometer as described by Pichlmayer et al. [14]. Finely powdered samples were burned in an elemental analyser (Carlo Erba Nitrogen Analyser 1500). The released N<sub>2</sub> was separated by a gas-chromatographic column from the other gases and introduced via a gas-splitting interface into the mass spectrometer (Finnigan MAT 251). The relative abundance of the stable isotopes of nitrogen (<sup>14</sup>N, <sup>15</sup>N) was measured against the air as standard. The results were calculated as  $\delta$  values as follows:

$$\delta^{15}$$
N (%o) = [( $R_{\text{sample}}/R_{\text{standard}}) - 1$ ] 1 000 (1)

where  $R_{\text{sample}}$  is  ${}^{15}\text{N}/{}^{14}\text{N}$  – ratio of sample and  $R_{\text{standard}}$  is  ${}^{15}\text{N}/{}^{14}\text{N}$  – ratio of standard (air).

# **2.3.** Calculation of N-amounts in the topsoil and the N-balance

Nitrogen concentrations in the soil were converted to soil N amounts by the following steps. Bulk density of the soil was determined for each treatment in 1956, 1975 and 1991, and values were interpolated using linear regression to give yearly values. The bulk densities were used to calculate the mass of soil in the top 0-20 cm. The inorganic portion of the soil, i.e. the whole soil minus the organic matter of the soil, was assumed to be constant during the experiment, and the amount of inorganic soil in the 0-20-cm layer in 1956 was used as a reference value. If the bulk density decreased, i.e. the soil volume increased, soil from below a depth of 20 cm had to be added to the 0-20-cm layer to give the same amount of inorganic soil as in 1956. Soils between 20 and 25 cm were sampled in 1991 and N concentrations were analysed. Because concentration of N in the subsoil (20-25 cm) of the different treatments was similar, we assume that the N concentration in this layer did not change significantly over time. The amount of N in the quantity of subsoil required to give the same mass of inorganic soil as in 1956 was added to the amount of N present in the 0-20cm layer. The nitrogen balance was calculated using the following formula:

$$N_{l} = N_{f} + N_{d} + N_{b} - \Delta N_{s} - N_{p}$$
<sup>(2)</sup>

where  $N_1$  is the annual loss of nitrogen from the topsoil (kg ha<sup>-1</sup>),  $N_f$  is the fertiliser N input (kg ha<sup>-1</sup> year<sup>-1</sup>),  $N_d$  is the annual wet and dry deposition (kg ha<sup>-1</sup>, according to [12]), N<sub>b</sub> is the non-symbiotic biologically fixed N (kg ha<sup>-1</sup> year<sup>-1</sup>),  $\Delta N_s$  is the annual change in the nitrogen inventory in the topsoil (kg  $ha^{-1}$ ) and  $N_p$  is the plant uptake (kg ha<sup>-1</sup>). The form of N storage in soil does not at all affect the overall N balance, which can only describe input and output. Interlayer ammonium, therefore, as well as microbial biomass has not been considered. N<sub>b</sub> was obtained using data on the relative potential N fixing activity of the respective treatment in a previous experiment [13] related to the maximum activity observed in the animal manure treatment. Absolute amounts were calculated by multiplying the relative activities with 15 kg N ha<sup>-1</sup> year<sup>-1</sup>, which was assumed to be the maximum amount of N fixed under the prevailing climatic conditions [6]. This is slightly lower than reported by Jenkinson [9] from the Broadbalk experiment in Rothamsted.

### 2.4. Calculation of N fractions and N turnover

To describe turnover rates of nitrogen in the experimental plots a simple first-order kinetic model was applied:

$$\frac{dN_r}{dt} = -\lambda \cdot N_r \tag{3}$$

where  $N_r$  is the remaining nitrogen in soil of the yearly N input ( $N_i = N_f + N_d + N_b$ ). Integration of equation (3) gives the exponential rate of decomposition for a single

fertiliser application, where  $\lambda$  is ln2 divided by the turnover half-life:

$$N_r = N_i \cdot e^{-\lambda t} \tag{4}$$

A continuous N fertiliser input can be described by equation (5):

$$N_r = N_i \int_0^t e^{-\lambda t} dt$$
 (5)

Integration of equation (5) from 0 to time t yields equation (6):

$$N_{diff} \approx N_r = N_i \cdot \left| \frac{1}{\lambda} - \frac{1}{\lambda} \cdot e^{-\lambda t} \right|$$
 (6)

Equation (6) was used to calculate turnover half-lives of the fertiliser nitrogen fractions in soil. Assuming that  $N_r$  is approximated by the difference ( $N_{diff}$ ) of the N content of the amended soil minus the N content of the no-N soil,  $N_i$  is approximated by the difference in the N input of the amended soil minus the N input of the no-N soil and t is 35 years, all parameters are known except the decomposition rate constant ( $\lambda$ ).  $\lambda$  can be determined using an iterative method.

Assuming equilibration of the system (t  $\rightarrow \infty$ ,  $e^{-\lambda t} \rightarrow 0$ ), that means N input equals N output, the turnover half-lives can be directly calculated:

$$N_{\rm diff} = N_{\rm i} \cdot \frac{1}{\lambda} \Longrightarrow \lambda = \frac{N_{\rm i}}{N_{\rm diff}}$$
(7)

The nitrogen content of the fertiliser in soil derived from isotopic data was calculated adopting the procedure described by Puget et al. [17]:

$$\mathbf{N}_{\rm fr} = \left| \frac{\left( \boldsymbol{\delta}_{\rm s} - \boldsymbol{\delta}_{\rm Ref.} \right)}{\left( \boldsymbol{\delta}_{\rm Fert} - \boldsymbol{\delta}_{\rm Ref.} \right)} \right| \cdot \mathbf{N}_{\rm T}$$
(8)

where  $\delta_{i}$  is  $\delta^{15}N$  value (‰) of the fertiliser-treated soil,  $\delta_{Ref.}$  is  $\delta^{15}N$  value (‰) of the no-N soil,  $\delta_{Fert}$  is  $\delta^{15}N$  value (‰) of the applied fertiliser,  $N_{T}$  is the total nitrogen content in the topsoil and  $N_{fr}$  is the nitrogen fraction originating from the fertiliser nitrogen. A slightly overestimated uncertainty of  $N_{fr}$ ,  $e_{fr}$  was obtained using the following equation proposed by Puget et al. [17]:

$$\mathbf{e}_{\mathrm{fr}} = \left[ \frac{\left( \delta_{\mathrm{s}} - \delta_{\mathrm{Ref.}} + \mathbf{e}_{\mathrm{s}} + \mathbf{e}_{\mathrm{Ref.}} \right)}{\left( \delta_{\mathrm{Fert}} - \delta_{\mathrm{Ref.}} \right)} \right] \cdot \mathbf{e}_{\mathrm{T}} + \left[ \frac{\left( \mathbf{e}_{\mathrm{s}} + \mathbf{e}_{\mathrm{Ref.}} \right)}{\left( \delta_{\mathrm{Fert}} - \delta_{\mathrm{Ref.}} \right)} \right] \cdot \left( \mathbf{e}_{\mathrm{T}} + \mathbf{N}_{\mathrm{T}} \right)$$
(9)

where  $e_s$ ,  $e_{Ref}$ ,  $e_{Fert}$  are the standard deviations of the respective  $\delta$  values and  $e_T$  is the standard deviation of the  $N_T$  measurement.

Turnover half-lives of nitrogen derived from fertiliser were calculated from isotopic data using equations (6) (35 years) and (7) (assuming equilibration), where  $N_{diff}$ is the amount of nitrogen in the soil derived from equation (8) (=  $N_{fr}$ ) and  $N_i = N_{fr}$ .

### **3. Results and discussion**

#### 3.1. Nitrogen in topsoils and N balance

Soil characteristics in the experimental plots were distinctly altered by the different treatments (*table I*). The application of peat, sewage sludge and ammonium sulphate resulted in a significant decrease in the pH values, which has already been discussed in detail in Kirchmann et al. [11]. Both organic carbon and N<sub>t</sub> contents were clearly affected by the fertiliser and manure applications (*table I*, *figure 1*). The bare fallow plot exhibited a remarkable decrease in nitrogen contents as compared with 1956 (0.16% N<sub>t</sub>) ending up with 0.11% in



**Figure 1.** Average  $N_1$  contents of topsoils (0–20 cm) of the Ultuna long-term field experiment during the first 38 years (treatments: fallow; no-N; green manure; animal manure; peat).

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Table I. Mean soil characteristics in 1993, 37 years after the start (autumn 1956) of four replicate field plots,  $\delta^{15}N$ values (mean of two to four plots) and mean composition of the organic amendments and mineral fertilisers (± standard deviations).

			Organic amendments and mineral fertilisers							
Treatment	pH in water	Organic C /g kg <sup>-1</sup>	Total N /g kg <sup>-1</sup>	C/N	δ <sup>15</sup> N /%0	Bulk density /kg dm <sup>-3</sup>	Organic ( /g kg <sup>-1</sup>	C Total N /g kg <sup>-1</sup>	C/N /‰	δ <sup>15</sup> N
Fallow	$6.3 \pm 0.1$	9.8 ± 0.1	$1.1 \pm 0.0$	8.9	$9.2 \pm 0$	.1 1.34	_	-	_	
No-N	$6.5 \pm 0.1$	$11.6 \pm 0.3$	$1.3 \pm 0.1$	8.9	$8.9 \pm 0.1$	.1 1.42	_	_	_	
Green manure	$6.3 \pm 0.1$	$16.4 \pm 1.2$	$1.7 \pm 0.0$	9.6	$8.0 \pm 0.8$	.1 1.34	$414 \pm 20$	$18.3 \pm 5.6$	22.6	$3.17 \pm 1.38$
Animal manure	$6.7 \pm 0.1$	$21.4 \pm 0.1$	$2.0 \pm 0.0$	10.7	$9.0 \pm 0.1$	.3 1.28	$395 \pm 42$	$17.6 \pm 3.0$	22.4	$7.63 \pm 1.37$
Peat	$5.8 \pm 0.2$	$30.6 \pm 1.3$	$1.7 \pm 0.0$	18.0	$5.9 \pm 0.1$	.2 1.16	$459 \pm 22$	$7.7 \pm 1.4$	69.6	$1.03 \pm 0.92$
Sewage sludge§	$5.8 \pm 0.1$	$24.2 \pm 1.8$	$2.5 \pm 0.2$	9.7	$7.0 \pm 0.0$	4 1.11	$304 \pm 18$	$32.9 \pm 2.3$	9.2	$4.45 \pm 0.21$
$Ca(NO_2)_2$	$6.9 \pm 0.1$	$14.9 \pm 0.6$	$1.6 \pm 0.1$	9.3	$6.0 \pm 0.0$	.4 1.34	_	171	_	1.4
(NH <sub>4</sub> ) <sub>2</sub> ŠÕ <sub>4</sub> <sup>§</sup>	$4.7\pm0.1$	$13.0\pm0.4$	$1.5 \pm 0.1$	8.7	$6.0 \pm 0.0$	.4 1.28	_	212	-	-1.8

Data for organic amendments are mean values from six different years (sewage sludge: two years). <sup>§</sup> Soil analysis from samplings in 1991.

	Fertiliser	Deposition*	Biologically	∆soil <sup>§</sup>	Plants	Losses in	
	(kg ha <sup>-1</sup> year <sup>-1</sup> )	(kg ha <sup>-1</sup> year <sup>-1</sup> )	$(kg ha^{-1} year^{-1})$	(kg ha <sup>-1</sup> year <sup>-1</sup> )	(kg ha <sup>-1</sup> year <sup>-1</sup> )	kg ha <sup>-1</sup> year <sup>-1#</sup>	% of N input
Fallow	0	10	4	-51	0	65	
No-N	0	10	7	-34	44	7	
Peat	31	10	10	7	41	17	33
Green manure	106	10	11	5	85	37	29
Animal manure	89	10	14	26	67	20	18
Sewage slugde	204	10	0	77	123	14	7
$Ca(NO_2)_2$	80	10	11	-18	90	29	29
$(NH_4)_2 SO_4$	80	10	0	-20	86	24	27

Table II. N-balance of the Ultuna long-term organic matter experiment (basis: year 1991).

\* Depositon was taken from Lövblad et al. [12].

<sup>§</sup> Annual change of total N in topsoil (basis: mineral soil mass in 0-20 cm in the year 1956).

<sup>#</sup> According to equation (2).

1994. Statistical analysis indicated that the highly significant decrease follows a linear regression  $(N_{t} = -0.0014 \text{ year} + 2.8081; R^{2} = 0.969 \text{ ***}),$ equilibrium between N mineralisation of the soil N pool and N deposition has, therefore, not yet been reached in the bare fallow plots. The same result was obtained for the no-N plots, although the N content of the topsoil remained on a higher level as compared to the fallow plots (% $N_t = -0.0008$  year + 1.7914;  $R^2 = 0.8091$  \*\*\*), despite the significant removal of N with the harvest (*table II*). Green manure-treated plots did not show any significant changes in N<sub>t</sub> contents in the topsoil. This is supported by the identical behaviour of Corg contents in this treatment [5]. Green manure was obviously able to keep the N<sub>t</sub> concentrations in the topsoil constant. Peat, animal manure and sewage sludge increased the N<sub>t</sub> contents of topsoils significantly (table I, figure 1). The effect of peat – due to the small amount of N introduced through peat amendments – was quite small. None of the five intensively investigated treatments – except green manure, where no trend was observed - showed a non-linear trend of N contents in the topsoil. This indicates that a much longer time-period is needed for equilibration than an observation period of 35–38 years. This is supported by the results of the Broadbalk experiment in Rothamsted, where the increase in N, contents in farmyard manure-treated plots started to level off approximately 50-60 years after the start of the experiment [15].

The mineral fertilisers,  $Ca(NO_3)_2$  and  $(NH_4)_2SO_4$  maintained the N<sub>1</sub> concentrations in topsoils, but not the total N inventory when taking into account soil bulk density changes (table II). In general, only green manure, animal manure and sewage sludge applications resulted in an increase in total nitrogen present in the mineral soil mass (0-20 cm) on the basis of the year 1956. The highest N losses calculated according to equation (2) were recorded in the bare fallow plots (*table II*). N losses were smallest for the no-N plots. The mineralisation of soil N (34 kg N ha<sup>-1</sup> year<sup>-1</sup>) and the N input by deposition and fixation of approximately 17 kg N ha<sup>-1</sup> year<sup>-1</sup> were only somewhat exceeding N removal by harvest. N losses from the other treatments showed the following ranking: green manure > calcium nitrate > ammonium sulphate > animal manure > peat > sewage sludge. Taking into account total N input alters the ranking (table II), peat being first followed by green manure and calcium nitrate. Losses from sewage sludge plots were remarkably low, although the N input was highest amongst all treatments.

Considering again the no-N treatment as reference, it was feasible to estimate the average fertili-

sation effect of the different treatments  $(N_f + N_b)$ on agricultural crops and removed with the harvest. Leaving out peat, which had a negative effect on N removal by plants, the following ranking was observed: ammonium sulphate (57 %) > calcium nitrate (55 %) > sewage sludge (40 %) > green manure (37 %) > animal manure (24 %). The availability of N introduced by peat, or even the induced N immobilisation by this treatment makes it clear that peat adds stable N forms to soil but cannot be considered as a N fertiliser. The N recovery from mineral fertilisers plus fixation reached the same magnitude as reported for fertiliser utilisation by several authors from <sup>15</sup>N labelling experiments although these are not directly comparable with results obtained by the difference method. A literature overview by Bhogal et al. [1] showed a range of 46.6–61% N from fertiliser recovered by wheat or barley (median: 58.9 %, n = 14). The lower average N recovery from organic amendments in our experiment was not due to larger N losses from mineral fertilisers but to the supply of more stable N fractions by the manure, which substituted the N amount mineralised from native soil N and on top of that increased the N inventory.



Figure 2. Average  $\delta^{15}$ N-values (‰) of soil organic matter of the topsoils of the Ultuna long-term field experiment during the first 38 years (treatments: fallow; no-N; green manure; animal manure; peat).

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### 3.2. <sup>15</sup>N abundances

The natural abundance of <sup>15</sup>N varied distinctly with time (figure 2), while changes seemed to have a general pattern and were followed by most treatments. One reason for that could be the generally considerable variation of  $\delta^{15}N$  in deposited N with time and space [8]. Compared with the  $\delta^{15}N$  values at the beginning of the experiment in 1956 (8.4-8.9 %) there was a clear change, which could be related to the amendments (figure 2). All mineral fertilisers and organic materials except animal manure exhibited significantly smaller  $\delta^{15}N$  values than the initial soil N pool. This was well reflected in soil samples after different time periods (table I, figure 2). Quantification of this quite obvious effect, however, was only feasible for green manure and peat because of the larger data set available. Using equation (8) and averaging over 5-7 years it was possible to estimate the contribution of fertiliser N to N, in the topsoil using the no-N treatment as reference (table III). A reference treatment is necessary in such cases to take into account changes in the natural abundance of <sup>15</sup>N due to other factors such as changes in the isotopic composition of the atmospheric input or isotopic shifts caused by microbial activity [3]. Uncertainties, nevertheless were quite high owing to the small isotopic differences between reference plots and treatments and the variation in values from sampling to sampling. On the other hand, it was possible to support the consistency of the data by a highly significant linear correlation between experimental years and contribution of peat N and manure N to N, in the topsoil. The calculated N portion from green manure or peat can be considered as an already stable N fraction. The stable N input of green manure was approximately 22 kg ha<sup>-1</sup> year<sup>-1</sup> (versus 39 kg N ha<sup>-1</sup> year<sup>-1</sup> according to the difference method), which is 20% of the total N input through this treatment. The respective values for peat were 31 kg ha<sup>-1</sup> year<sup>-1</sup> (versus 27 kg N ha<sup>-1</sup> year<sup>-1</sup>) and 102 %. The latter result indicated that N contained in peat was just stored in the soil and did not contribute to the plant uptake or losses, both of which were therefore derived from mineralisation of native soil N and wet and dry deposition of nitrogen. This result is corroborated by the high C/N ratio of peat of approximately 70. This low decomposability was already mentioned as one of the main reasons for organic matter piling up in the peat plots [5] resulting in a seven times lower microbial biomass related to the Corg content of the soil as compared to the other treatments [22].

 $\delta^{15}$ N values of selected plant samples were determined and ranged from 1.8 to 10.4 ‰. The well-known effect of isotopic shifts due to selective N uptake of N compounds of different isotopic signature by plant roots from soil [8] did not allow

**Table III.** Contribution of fertiliser N to  $N_t$  in the topsoil as derived from changes in the <sup>15</sup>N abundance in the experimental plots.

Contribution of fertiliser N to $N_t$ ; average $\pm$ standard deviation <sup>§</sup>										
<i>I</i>	Average 75–79		Average 81–87	Average 88–94 (%)			Average stable N input			
(%)			(%)				kg ha <sup>-1</sup> year <sup>-1</sup> (56–94)	% of $N_t$ applied through fertiliser		
Green manu	ire –	+/	12	+/	15	+/	22	20		
Peat	14	-13	17	-3	24	-12	31	102		

§ According to equations (8) and (9).

quantification of the contribution of fertiliser or manure N to N uptake into crops.

### 3.3. Turnover half-lives

Table IV shows the increase in soil N inventory in relation to the no-N reference plots. According to equations (6) and (7) it is possible to use the difference between reference plots and treatments to estimate the turnover half-lives of the additional N input through treatments (mainly applied fertiliser N). The shortest half-lives (HL) were derived for the mineral fertilisers, the longest HL for the hardly decomposable organic substance peat. Half-lives of the two mineral fertilisers did not differ. Therefore, processes which might influence the N turnover of differing N sources (NO<sub>3</sub>, NH<sub> $\lambda$ </sub>), such as ammonium fixation in interlayers of clay minerals for example, were of no significant impact. This result is in line with other field experiments conducted in Sweden [18]. Green manure exhibited the shortest half-life of nitrogen input amongst all organic amendments. In some cases (peat, animal manure, sewage sludge) a distinct difference between the iterative calculation of the HL (equation (6)) and the method assuming equilibrium (equation (7)) occurred, the latter values being

shorter than the former. This is a strong indication that equilibrium has not yet been reached for these treatments. A very large difference was obtained for peat N, which leads to the conclusion that the peat N, in particular, is highly stable and exhibited a more or less inert behaviour during the time span of the experiment. Taking into account the isotopic changes the peat and green manure plots led to deviating results concerning half-lives. In the case of peat we observed an even longer half-life than with the difference method. This matches with the fact that peat N was not lost at all during the experimental period (table III). The green manure N behaved exactly the reverse. The isotopic method showed a considerably shorter HL for green manure nitrogen already in equilibrium. The calculated HL of 5 years is much closer to the value observed for <sup>15</sup>N-labelled grass/clover residues of  $\approx 2$  years after a single application in New Zealand (calculated from [7]). This implies that the observed positive difference in the N inventory in the green manure-treated plots compared to the no-N reference plots is only partly due to input of stable green manure N. In addition it seems that applying green manure considerably decreased the mineralisation of the original soil N. A similar effect can be assumed for the mineral fertiliser

Γ	Difference method			Isotopic method ( <sup>15</sup> N abundances)				
	N increase*	Turnover half-lives (years)		N increase*	Turnover half-lives (years)			
	%	Α	В	%	A	B		
Peat	25	51	19	29	ş	24		
Green manure	37	9	9	21	5.0	5.0		
Animal manure	e 56	24	15					
Sewage sludge	104	19	14					
$Ca(NO_2)_2$	15	5	5					
$(NH_4)_2 SO_4$	13	5	5					

**Table IV.** Turnover half-lives of N input through treatments derived from the difference method and turnover half-lives of fertiliser N derived from the isotopic method.

A assuming an exponential rate of decomposition (35 years of application); equation (6).

B assuming an equilibrium of N input and output; equation (7).

\* Build-up of soil N relative to the no-N reference plot.

<sup>§</sup> Value cannot be deduced after 35 years owing to high stability of N in peat.

nitrogen because the half-life values obtained by the difference method for these treatments seem to be too high.

### 4. Conclusion

Green manure, animal manure and sewage sludge increased the amount of N present in the 0–20-cm topsoil layer on the basis of constant mineral soil mass since 1956.

N losses were highest for mineral fertilisers and green manure and very low for the no-N plots.

Mineral N fertilisers exhibited the highest N use efficiency.

The <sup>15</sup>N abundance of soil was altered by fertiliser and manure N input. The 'stable' N portion could be deduced for green manure (20% of input) and peat ( $\approx 100$ %).

Mineral fertilisers showed relatively short halflives for applied N; N input and N output were already in equilibrium after the time elapsed from the start of the experiment.

Equilibration between N input and N output was not observed in plots receiving organic amendments. Peat N showed a more or less inert behaviour during the time span of the experiment owing to its high stability.

The <sup>15</sup>N abundance method added valuable information to the results obtained by the traditional difference method using the no-N treatment as reference.

Acknowledgements: We thank the Austrian Science Foundation (Fonds zur Förderung der wissenschaftlichen Forschung) for financing this bilateral project. The authors thank Pär Hilsström for the careful and responsible maintenance of the long-term experiment.

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