

# **Nitrogen regime of two bulgarian soils after 30 years of mineral and organic-mineral fertilisation ( $^{15}\text{N}$ study).**

*Statut azoté de deux sols bulgares après 30 ans de fertilisation minérale et organique (essais avec  $^{15}\text{N}$ ).*

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## **Abstract**

The objective of this study is to determine some changes in the nitrogen regime of soils with long-term mineral and organic mineral fertilisation. The investigations have been carried out on two major Bulgarian soils : leached smolnitza (vertisol) and grey forest soil. Three treatments of long-term (30 years) mineral and organic-mineral fertilisation have been studied : 1. PK ; 2. NPK ; 3. NPK + farmyard manure (FYM - every other year). A modification of the method of Stanford-Smith for determination of soil nitrogen mineralisation potential based on the isotope dilution method has been worked out, taking into account the effect of applied mineral nitrogen fertilizers on the additional mineralisation of soil organic nitrogen. Microfield and pot experiments with maize and wheat have been carried out.

***Keywords :*** *long-term fertilisation, nitrogen mineralisation potential, isotope dilution method.*

## **Résumé**

L'objectif de cette étude était de déterminer les changements dans le « statut azoté » de sols recevant des fertilisations minérales et organiques sur une longue période. Les essais ont été conduits sur deux sols typiques bulgares : un sol lessivé Smolnitza (vertisol) et un sol gris de forêt. Trois traitements de fertilisation longue durée (30 ans) minérale et organo-minérale ont été comparés : 1. PK ; 2. NPK ; 3. NPK + fumier. Une adaptation de la méthode de Stanford-Smith pour la détermination du potentiel de minéralisation de l'azote du sol a été proposée, basée sur la méthode de dilution isotopique. Des essais en microparcelles ainsi que des incubations en pots avec maïs et blé ont été poursuivis.

**Mots-clés :** essais fertilisation longue durée, potentiel de minéralisation de l'azote, méthode de dilution isotopique.

## 1. Introduction

Intensive arable farming faces several problems related to both soil fertility and environment (Broussaard et al. 1988). Among these urgent problems are the contamination of ground and surface water and the atmosphere, due to intensive use of fertilisers. One of the changes in farming practices proposed involves a partial replacement of mineral fertilisers by manure (Laanbroek H.J. and S. Gerards, 1991). Problems with organic fertilisers are possible too. Ammonium might be produced from manure at times when there is no need for mineral N by the plants. The following nitrification may lead to undesired effects on the environment, i.e., leaching of nitrate into ground water or the production of N-oxides by denitrifying bacteria.

Long-term applications of mineral and organic fertilisers open into significant changes in soil characteristics. The parameters of these characteristics vary considerably depending on the type of the soil-fertiliser-plant system.

The objective of this study is to determine some important for agriculture and environment changes in the nitrogen regime of soils with long-term mineral and organic mineral fertilisation.

## 2. Materials and methods

| Soil<br>Treatment | Leached smolnitza |                |                  |     |     | Grey forest soil |                |                  |     |     |
|-------------------|-------------------|----------------|------------------|-----|-----|------------------|----------------|------------------|-----|-----|
|                   | Total<br>N%       | Organic<br>C % | C:N              | pH  |     | Total<br>N%      | Organic<br>C % | C:N              | pH  |     |
|                   | H <sub>2</sub> O  | KCl            | H <sub>2</sub> O | KCl |     | H <sub>2</sub> O | KCl            | H <sub>2</sub> O | KCl |     |
| *Soil - 1960      | 0.159             | 1.78           | 11.2             | -   | 5.5 | 0.134            | 1.29           | 9.2              | -   | 4.4 |
| PK                | 0.142             | 1.79           | 11.9             | 6.1 | 5.0 | 0.128            | 1.12           | 8.8              | 5.9 | 4.9 |
| NPK               | 0.160             | 1.89           | 12.7             | 5.6 | 4.7 | 0.138            | 1.23           | 8.9              | 5.8 | 4.9 |
| NPK + FYM         | 0.212             | 2.44           | 11.5             | 6.1 | 5.3 | 0.171            | 1.62           | 9.5              | 5.4 | 4.4 |

\*Soil - 1960 - Data by Dinchev,1983

*Table 1.  
Soil characteristics of long-term fertilised soil (30 years)*

| Soils             | Content of particles % |            |
|-------------------|------------------------|------------|
|                   | < 0,01 mm              | < 0,001 mm |
| Leached smolnitza | 71.4                   | 53.9       |
| Grey forest soil  | 50.4                   | 28.5       |

*Table 2.  
Texture of studied soils*

The investigations have been carried out on two major Bulgarian soils: leached smolnitza (Pellic Vertisol, FAO) and grey forest soil (Orthic Luvisol, FAO). The texture of the leached smolnitza is clay and the texture of the grey forest soil is silty silt. Three treatments of long-term (30 years) mineral and organic-mineral fertilisation have been studied: 1. PK; 2. NPK; 3. NPK+ Farmyard manure (FYM - every other year). Fertiliser's rates were 200 kg N.ha<sup>-1</sup>, 140 kg P<sub>2</sub>O<sub>5</sub>. ha<sup>-1</sup>, 120 kg K<sub>2</sub>O.ha<sup>-1</sup> and 40 tons farmyard manure per hectare. In experimental year farmyard manure have been applied on the grey forest soil before the maize.

### **Laboratory incubation experiment**

A modification of the method of Stanford-Smith for determination of soil nitrogen mineralisation potential based on the isotope dilution method (Fried and Dean, 1952) have been worked out, taking into account the effect of applied mineral nitrogen fertilisers on the additional mineralisation of soil organic nitrogen. The nitrogen mineralisation potential of the soils was determined by Stanford-Smith's method, 1972 and by our own modification of this method. The modification of method consists in the addition of  $^{15}\text{N}$  labelled nitrogen fertiliser (ammonium nitrate). No initial washing of the soil was done as to make possible soil incubation with ammonium nitrate. During the first two weeks soil moisture was 80% of field capacity. Throughout this period the fertiliser nitrogen have been incorporated into soil's cycle. Triplicate 15-g samples of soil and equal weights of quartz sand mixed thoroughly moistened for the PK treatment to 80% of FC and moistened and fertilised with 67 mg N.kg $^{-1}$  soil for the NPK and NPK+FYM treatments. The soil was retained in the 50-ml leaching tube by means of a glass wool pad. A thin glass wool pad was placed over the soil to avoid dispersing the soil when solution was poured into the tube. Present mineral N was removed by leaching with 100 ml of 0.01M CaCl $_2$ , followed by 25 ml of a nutrient solution devoid of nitrogen. Excess water was removed under vacuum. Tubes were incubated at 35°C for periods of 2, 4, 8, 12, 16, 22 and 30 weeks with intermittent leachings of mineral nitrogen.

### **Micro field experiments**

The micro field experiment was carried out on the leached smolnitzia with wheat and on the grey forest soil with maize. Micro plots of 1 m $^2$  in the PK, NPK and NPK+FYM treatments have been used in the experiment. Same rate for fertilising have been used - 200 kg N.ha $^{-1}$  representing 20 g N per m $^2$ .

### **Pot experiments**

The pot experiment was carried out in 20 kg pots with maize and wheat as test crops on the two studied soils. The soils from the PK, NPK and NPK+FYM treatments have been used. The fertiliser rate evaluated for 1 kg soil - 67 mg N.kg $^{-1}$  soil has been applied.

The soil samples for pot and incubation experiments have been collected from the surface 30 cm depth of the three studied treatments of every soil. Labelled nitrogen have been applied as ammonium nitrate with % $^{15}\text{N}$  atom excess: 10% for the micro field experiment; 5 % for the pot experiment and 28% for the incubation experiment.

## **3. Results and discussion**

Changes in the soil pH were found between treatments in both soils. Acidification of soil has been observed in PK and NPK treatments of leached smolnitzia and in NPK+FYM treatment of grey forest soil.

Long-term organic-mineral nitrogen fertilisation caused an increase in total nitrogen and organic carbon content (Table 1). The nitrogen mineral fertilisation had stopped the nitrogen fertility degradation. No changes have been observed in total nitrogen content in NPK treatment. Parallel application of mineral nitrogen and organic matter increased total nitrogen content as well as organic carbon content. Compared to the control (1960) total nitrogen decreased by 12% in PK treatment in leached smolnitza and by 5% for grey forest soil, not changed for NPK treatment and increased by 33% for NPK+FYM treatment in leached smolnitza and by 28% in grey forest soil. Compared to the control (1960) organic C increased by 6% for NPK treatment in leached smolnitza and by 10% in grey forest soil, organic C increase for NPK+FYM treatment was 36% for leached smolnitza and 45% for grey forest soil. Our results agree with related findings of other workers (Anderson and Peterson, 1973, Campbell 1978). The lower organic matter build up in leached smolnitza is mainly due to the relatively high level of organic matter already present in the soil. The C:N ratio increases on the leached smolnitza in mineral fertilising treatment and in organic - mineral fertilising treatment on grey forest soil.

Results have been obtained showing the available nitrogen and nitrogen mineralisation potential to increase under the influence of both the nitrogen fertilisers in the year of application and the long-term nitrogen fertilisation (Table 3). Values of the nitrogen mineralisation potential and the available nitrogen obtained by isotope dilution method were similar. The mineralisation potential, defined as amount of N susceptible to mineralisation in infinite time, ranged from 249 to 506 mg N.kg<sup>-1</sup> for the leached smolnitza and from 204 to 284 mg N.kg<sup>-1</sup> for the grey forest soil. The NPK+FYM treatments showed a stronger effect on the nitrogen mineralisation potential than NPK application, and this was related to the increasing organic carbon in soil. Campbell et al., 1986 also observed a sharp increase of potentially mineralisable nitrogen in fields where farmyard manure was applied regularly over a long period of time. The heaviest texture, favourable to organic matter stabilisation in soil, in the leached smolnitza had enabled higher nitrogen accumulation in readily decomposable N pool. According to Faurie (1980) large changes in the labile organic matter fraction are associated with high microbial biomass and nitrogen availability. The half part of the total nitrogen increase due to the farmyard manure application on leached smolnitza was found in nitrogen mineralisation potential pool, for the grey forest soil the increase of a nitrogen mineralisation potential represents a quarter part from total nitrogen increase. Therefore the plant accessible nitrogen pool increase in leached smolnitza significantly and nitrogen nutrition regime of soil became more favorable for plant development.

| Treatment         | * Soil N mg.kg <sup>-1</sup> | ** Fertiliser N mg.kg <sup>-1</sup> | Available N mg.kg <sup>-1</sup> | N pot mg.kg <sup>-1</sup> |
|-------------------|------------------------------|-------------------------------------|---------------------------------|---------------------------|
| Leached smolnitza |                              |                                     |                                 |                           |
| PK                | 174                          | -                                   | -                               | 249                       |
| NPK               | 306                          | 54                                  | 380                             | 367                       |
| NPK + FYM         | 395                          | 52                                  | 509                             | 506                       |
| Grey forest soil  |                              |                                     |                                 |                           |
| PK                | 164                          | -                                   | -                               | 204                       |
| NPK               | 192                          | 62                                  | 257                             | 232                       |
| NPK + FYM         | 232                          | 58                                  | 299                             | 284                       |

\* Soil N - Soil nitrogen mineralised and leached for 30 weeks of incubation

\*\* Fertiliser N - Fertiliser nitrogen leached for 30 weeks of incubation

*Table 3*

*Changes in available nitrogen in soil after 30 years mineral and organic-mineral fertilising, determined by Stanford and Smith (1972) method (N pot - nitrogen mineralisation potential) and isotope dilution method (Available N).*

The dry matter yield of wheat and maize and the nitrogen uptake with plants from pot and micro field experiments were higher in the organic-mineral fertilisation treatment. The better conditions for plant growing in the leached smolnitza reflected in about 50% increase in that treatment of dry matter yield and nitrogen uptake in the pot experiment with wheat (Table 4). The same treatment on grey forest soil increased the yield and nitrogen uptake 5-fold.

| Treatments        | Dry matter yield g per pot | Nitrogen uptake mg.kg <sup>-1</sup> |              |        | A value mg N.kg <sup>-1</sup> | FUE % | Ndff % |
|-------------------|----------------------------|-------------------------------------|--------------|--------|-------------------------------|-------|--------|
|                   |                            | N soil                              | N fertiliser | N sum. |                               |       |        |
| Leached smolnitza |                            |                                     |              |        |                               |       |        |
| PK                | 127.6                      | 65                                  | -            | 65     | -                             | -     | -      |
| NPK               | 164.5                      | 74                                  | 41           | 115    | 119                           | 61.1  | 35.6   |
| NPK+FYM           | 177.7                      | 94                                  | 43           | 137    | 145                           | 64.2  | 31.4   |
| Grey forest soil  |                            |                                     |              |        |                               |       |        |
| PK                | 32.3                       | 15                                  | -            | 15     | -                             | -     | -      |
| NPK               | 146.3                      | 41                                  | 40           | 81     | 69                            | 59.7  | 49.4   |
| NPK+FYM           | 152.1                      | 47                                  | 40           | 87     | 79                            | 59.7  | 46.0   |

*Table 4*  
*Pot experiment with wheat*

| Treatments        | Dry matter yield g per pot | Nitrogen uptake mg.kg <sup>-1</sup> |              |        | A value mg N.kg <sup>-1</sup> | FUE % | Ndff % |
|-------------------|----------------------------|-------------------------------------|--------------|--------|-------------------------------|-------|--------|
|                   |                            | N soil                              | N fertiliser | N sum. |                               |       |        |
| Leached smolnitza |                            |                                     |              |        |                               |       |        |
| PK                | 132.5                      | 45                                  | -            | 45     | -                             | -     | -      |
| NPK               | 248.5                      | 76                                  | 41           | 117    | 126                           | 61.2  | 35.0   |
| NPK+FYM           | 252.8                      | 140                                 | 39           | 179    | 243                           | 59.1  | 21.8   |
| Grey forest soil  |                            |                                     |              |        |                               |       |        |
| PK                | 60.0                       | 17                                  | -            | 17     | -                             | -     | -      |
| NPK               | 209.1                      | 57                                  | 43           | 100    | 87                            | 64.2  | 43.0   |
| NPK+FYM           | 244.2                      | 65                                  | 40           | 105    | 109                           | 59.7  | 38.1   |

*Table 5*  
*Pot experiment with maize*

| Treatments | Leached smolnitza |              |        | Grey forest soil |              |        |
|------------|-------------------|--------------|--------|------------------|--------------|--------|
|            | N soil            | N fertiliser | N sum. | N soil           | N fertiliser | N sum. |
| PK         | 39                | -            | 39     | 32               | -            | 32     |
| NPK        | 34                | 3            | 37     | 31               | 2            | 33     |
| NPK+FYM    | 36                | 3            | 39     | 35               | 2            | 37     |

*Table 6  
Residual inorganic nitrogen after wheat in soil of pot experiment mg.N.kg<sup>-1</sup>*

| Treatments | Leached smolnitza |              |        | Grey forest soil |              |        |
|------------|-------------------|--------------|--------|------------------|--------------|--------|
|            | N soil            | N fertiliser | N sum. | N soil           | N fertiliser | N sum. |
| PK         | 28                | -            | 28     | 21               | -            | 21     |
| NPK        | 22                | 2            | 24     | 19               | 2            | 21     |
| NPK+FYM    | 46                | 6            | 52     | 23               | 2            | 25     |

*Table 7.  
Residual inorganic nitrogen after maize in soil of pot experiment mg.N.kg<sup>-1</sup>*

Results for yield and nitrogen uptake are not in correlation with mineralisation potential. Coefficient of fertiliser use efficiency (FUE) was higher on the leached smolnitza. The half of the nitrogen uptake by plants on grey forest soil has been derived from fertiliser. In the conditions of leached smolnitza the nitrogen derived from fertiliser (Ndff) was about 30 - 35%.

The results obtained in the pot experiment with maize show that maize uses much better the soil nitrogen (Table 5). Yields in nitrogen fertilised treatments on leached smolnitza were nearly equal. On grey forest soil the organic - mineral nitrogen fertilising has been ensured yield of maize to increase to 244.2 g per pot. That yield is similar as on the leached smolnitza (252.8 g per pot). That's why it is possible to make a conclusion for the optimised status of the nitrogen regime in organic - mineral treatment on two studied soils. The coefficients of fertiliser use efficiency for maize were similar as for the wheat. The result for Ndff in the treatment NPK+FYM on leached smolnitza 21.8% show that in the soil has been accumulated amounts of a soil nitrogen sufficient for the plant's development. In support of that is the nitrogen mineralisation potential of this treatment - 506 mg N.kg<sup>-1</sup> and highest amounts of inorganic nitrogen in soil after the end of experiment (Tables. 3, 7 ).

The interest on determining relative N mineralisation capacities of soils is related with residual nitrogen in soil after harvesting, too. In humid-region agriculture residual nitrogen is a potential environmental hazard. In dryland cereal farming, on the other hand, the accumulation of mineral N is significant in supplying N to the succeeding crop. Limited volume of soil in pot experiments is the factor determining the similar amounts of residual nitrogen in soil, except the NPK+FYM treatment of maize on leached smolnitza (Tables 6, 7 ).

| Treatments | Dry matter yield g. m <sup>-2</sup> | Nitrogen uptake mg.m <sup>-2</sup> |              |        | A value mg N.kg <sup>-1</sup> | FUE % | Ndff % |
|------------|-------------------------------------|------------------------------------|--------------|--------|-------------------------------|-------|--------|
|            |                                     | N soil                             | N fertiliser | N sum. |                               |       |        |
| PK         | 905                                 | 9742                               | -            | 9742   | -                             | -     | -      |
| NPK        | 1854                                | 18114                              | 9024         | 27138  | 57                            | 45.1  | 33.3   |
| NPK+FYM    | 1965                                | 20253                              | 9136         | 29389  | 63                            | 45.7  | 31.1   |

*Table 8.  
Wheat micro field experiment on leached smolnitza*

| Treatments | Dry matter yield g. m <sup>-2</sup> | Nitrogen uptake mg.m <sup>-2</sup> |              |        | A value mg N.kg <sup>-1</sup> | FUE % | Ndff % |
|------------|-------------------------------------|------------------------------------|--------------|--------|-------------------------------|-------|--------|
|            |                                     | N soil                             | N fertiliser | N sum. |                               |       |        |
| PK         | 783                                 | 6141                               | -            | 6141   | -                             | -     | -      |
| NPK        | 1662                                | 17060                              | 4040         | 21100  | 103                           | 20.2  | 19.1   |
| NPK+FYM    | 1970                                | 18707                              | 5796         | 24503  | 79                            | 29.0  | 23.7   |

*Table 9  
Maize micro field experiment on grey forest soil*

The 30 years of organic-mineral fertilising ensure higher yields and nitrogen uptake in NPK+FYM treatment in micro field experiments with wheat and maize. In conditions of micro field experiments the coefficients of fertiliser use efficiency decreased with 25% for the wheat and 2 - 3 fold for maize compared to pot experiment conditions (Tables 8, 9 ).

Residual mineral nitrogen amounts are shown in Tables 10 and 11. Differences are due to soil type, crop properties and differences in water temperature regime of growing periods of wheat and maize.

The use of labelled nitrogen fertilisers allowed a comparison to be made of the results of soil nitrogen mineralisation potential determined by laboratory methods and the net nitrogen mineralisation in conditions of micro field and pot experiments with maize and wheat. The limited amounts of soil in the pot experiments make possibly the available nitrogen to be spent up more fully than in field conditions.

| Treatments | Soil depth, cm | N soil | N fertiliser | N sum. |
|------------|----------------|--------|--------------|--------|
| PK         | 0-30           | 17     | -            | 17     |
|            | 30-60          | 18     | -            | 18     |
| NPK        | 0-30           | 22     | 5            | 27     |
|            | 30-60          | 22     | 2            | 24     |
| NPK+FYM    | 0-30           | 24     | 3            | 27     |
|            | 30-60          | 26     | 2            | 28     |

*Table 10.  
Residual inorganic nitrogen in leached smolnitza after wheat harvest mg.N.kg<sup>-1</sup>*

| Treatments | Soil depth, cm | N soil | N fertiliser | N sum. |
|------------|----------------|--------|--------------|--------|
| PK         | 0-30           | 18     | -            | 18     |
|            | 30-60          | 18     | -            | 18     |
| NPK        | 0-30           | 37     | 7            | 44     |
|            | 30-60          | 22     | 2            | 24     |
| NPK+FYM    | 0-30           | 37     | 4            | 41     |
|            | 30-60          | 27     | 2            | 29     |

*Table 11.  
Residual inorganic nitrogen in grey forest soil after maize harvest mg.N.kg<sup>-1</sup>*

Introduction of the A-value (Fried and Dean, 1952) as an index of soil N availability has prompted considerable discussion regarding its merits and interpretations (Smith and Legg, 1971). The orthodox thesis that the A-value is a constant for a given soil did not be confirmed in our study. Irrespective of a great amount of soil used in the pot experiments (20 kg), the A-values differ substantially from those obtained in the field experiment. The A-values for wheat in pot experiments were similar as soil nitrogen uptake for maize (Tables 4, 5). It means than results for A-values in pot experiments with wheat as test crops were underestimated. The higher A-values obtained in the experiment with maize as a test crop, compared to those with wheat, enabled us to conclude that each obtained result is good for the soil-crop pair only.

#### 4. Conclusions

The results of this study show significant change of soil pH, total N, organic C and C:N ratio depending of soil type and used fertilisers (mineral or organic - mineral). Available nitrogen and nitrogen mineralisation potential increased under the influence of both the nitrogen fertilisers in the year of application and the long-term nitrogen fertilisation. The heaviest texture, favourable to organic matter stabilisation in soil, in the leached smolniza had enabled higher nitrogen accumulation in readily decomposable N pool. The dry matter yield of corn and maize and the nitrogen uptake with plants from pot and micro field experiments were highest in the organic-mineral fertilisation treatment. Coefficients for fertilizer use efficiency and nitrogen derived form fertiliser vary strongly in pot and field experiment. A-value determination of available soil nitrogen for a given soil is valid for studied soil-crop pair only. To maintain an optimal soil organic status and consequently optimal microbial activity for nutrient availability to plants, manures with the higher C content should be incorporated into soil.

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