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Nitrogen transformations in soil. Nitrates

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Abstract: N is a very important macronutrient for normal development of plants, its role being both structural and metabolic. The chain of cyclic transformations of N in nature includes atmospheric N fixation, mineralisation of organic matter, immobilisation of mineral N forms, nitrification of ammonium N, denitrification, volatilisation into atmosphere and leaching of nitrates from the soil.

The study is based on a detailed soil survey effectuated on the cadastral territory Orțisoara (Timiș county). It has been made 62 soil profiles and 248 soil samples were analysed. The paper discuss especially the N, NO_3, NO_2, humus content in the soil profiles and water. Losses of N via NH_3 volatilization can be 50 % of the N in animal slurries and manures can be lost in this way. They are N - fixing organisms, living free or in symbiosis with other lower organisms.

The most significant types of terrestrial N fixation are the legume / rhizobia symbiosis and the actinorhizal symbioses, genus Frankia. in aquatic system photosynthetic cyanobacteria such as Anabaena and Nostoc. The primary sources of soil organic matter are dead plants. The organic matter content of soils ranges from less than 1% in desert soils to close to 100% in organic soils. Most of the compounds are used as nutrient and energy sources for microbial growth. Humic substances are by nature highly complex mixtures, and the genesis takes place over a time scale of hundreds to thousands of years. Humic substances can be: humic acid; fulvic acid; humin. Nitrification is an aerobic process, autotrophic and heterothrophic. Autotrophic nitrification is dominant type in agricultural soils. The nitrate ion is extremely soluble in water and can easily be washed out of soil to natural waters by leaching and surface runoff. It can be concluded that there is now no medical evidence to suggest any link between nitrate intake and stomach cancer. Any nitrate escaping to streams, rivers, or lakes can increase the growth of water plants (algae) and thus alter the ecology of aquatic systems.

Plants in soil will preferentially assimilate $NO_3^- \rightarrow NO_2^- \rightarrow NH_4^+ \rightarrow N_2$. All the soil types analysed have a C/N ratio under value 25, the range is between 10.99 (Solonetz) and 15.07 (Vertisols).

The greatest values for Humus and N content are in the Phaeozems (3.93% Humus, 0.165% N), Vertisols (3.94% Humus, 0.152 % N) and Chernozems (3.21% Humus, 0.143 % N).

Vertisols are deep clayey soils (>45% clay) dominated by clay minerals such as smectites. N, NO_3^- and Humus are strongly adsorbed.

Natric horizon has a great clay content and a high amount of exchangeable sodium (30-50 %) and a pH 9-10.

Keywords: soil, nitrogen, organic matter, nitrates, nitrites.

1. INTRODUCTION

The amount of N in surface mineral soils generally ranges from 0.02 to 0.50% N. The N content in soils is closely related to the soil organic matter content, of which it makes up approximately 5 per cent. It is available to plants mainly in inorganic forms, as nitrate and ammonium, which usually represent < 1 % of the total soil N content. An appreciable fraction of the nitrogen content of subsoils and rocks occurs as NH_4^+ ions substituting for K^+ ions in micas, as revealed by NH_4^+ released by HF treatment of mineral fractions. Mineral – humus complexes also account for much additional nitrogen of soils that can be released HF treatment. A minor and transient source of available N is represented by certain simple organic compounds, especially those containing free amide and amino groups and nitrite. N is a very important macronutrient for normal development of plants, its role being both structural and metabolic. It is a constituent of proteins, enzymes, nucleic acids, chlorophyll pigments, vitamins and intermediary metabolic products involved in synthesis of substance and in transfer of energy. [6]

The chain of cyclic transformations of N in nature includes atmospheric N fixation, mineralisation of organic matter by micro – organisms, immobilisation of mineral N forms by micro-organisms and higher plants, nitrification of ammonium N by micro-organisms, reduction of nitrates by denitrification, volatilisation of gaseous N forms from the soil into atmosphere and leaching of nitrates from the soil. The natural cycle of N may be influenced by industrial emissions in the atmosphere and by fertiliser addition in the soil. [2]

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Global sources of available N [10]

Table 1

Source	Ncontent ($x10^{16}$kg)	Total (%)
Atmosphere	386000	87.00
Oceans and lakes		
-dissolved N_2	2190	0.50
-soluble inorganic N	0.11	0.02
Sediments	35000-55000	12.00
Sea bottom organic N	0.054	0.01
Terrestrial biosphere	0.028-0.065	0.01
Terrestrial soils		
-organic N	0.022	0.0050
-clay-fixed NH_4^+	0.022	0.0005

2. MATERIALS AND METHODS

The study is based on a detailed soil survey effectuated on the cadastral territory Ortisoara (Timis county). It has been made 62 soil profiles and 248 soil samples were analysed physical and chemical.

The paper discuss especially the N, NO_3, NO_2, humus content in the soil profiles and water. [11]

3. RESULTS AND DISCUSSIONS

The principal environmental and health concerns associated with N cycling in soil are the potential for trace gas production and its effect on global warming, the potential for nutrient loss, and the movement of N to environments where it can cause eutrophication and potential health problems. Losses of N via NH_3 volatilization can be 50 % of the N in animal slurries and manures can be lost in this way.

N_2 Fixation

Nitrogen fixation is a process by which a micro – organism or an association of micro – organisms reduce N_2 to NH_3. The micro – organisms are represented by photo – autotrophic and heterotrophic bacteria, blue – green algae and actinomycetes. They are N - fixing organisms, living free or in symbiosis with other lower organisms (fungi, mosses) or higher organisms (nonleguminous or leguminous plants.)

$$N_2 + 16Mg - ATP + 8H^+ \xrightarrow{Nitrogenase} 2NH_3 + H_2 + 16ADP + 16Pi + 16Mg^{2+}$$

The amount of soil – air content is directly related to the bulk density and the amount of water in the soil profile. The bulk density of soil varies from 1.0 Mg m^{-3} to 1.7 – 1.8 Mg m^{-3} ($Mg=10^6$g).

The soil pores or voids or air - filled porosity can vary between 30 and 60%

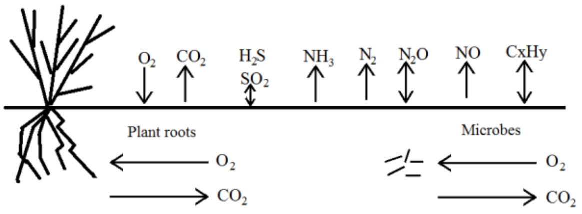

Figure 1. Flow directions of gases within soil

The most significant types of terrestrial N fixation are the legume / rhizobia symbiosis and the actinorhizal symbioses, genus Frankia. in aquatic system photosynthetic cyanobacteria such as Anabaena and Nostoc.

In some areas, lichens are responsible, in the boreal forests and arctic tundra. Legumes and the Ulmaceous are nodulated by unicellular bacteria known as Rhizobia, on species like: Phaseolus, Pisum, Cicer, Lotus, Lupinus, Trifolium, Medicago, etc.

The values for global N fixation may lie the range 100 – 200 Tg N ($Tg=10^{12}$gr) per year. [9]

Mineralisation and humification of organic matter

The primary sources of soil organic matter are dead plants in the form of leaves, straw, twigs, roots. Soil may contain several tons of organic matter per hectare, which consists of 15-60% cellulose, 10-30%, hemicelluloses, 5-30% lignin, and 2-15% protein. [7] Minor components are phenols, sugar, amino acids, and peptides.

The organic matter content of soils ranges from less than 1% in desert soils to close to 100% in organic soils. A typical agricultural soil may contain between 1 and 5 % in the top 15 cm. Most of the compounds are used as nutrient and energy sources for microbial growth. There are two categories of natural organic matter: labile (readily degrading) and resistant (slowly degrading). Plant debris may become resistant to microbial degradation by interaction with minerals whereas its completely humified products are produced by random condensation of refractory plant and microbial products. Humification – the alteration of biologically derived carbon to chemically complex forms – also represents a critical process driving carbon sequestration. [4]

Humic substances are by nature highly complex mixtures, and the genesis takes place over a time scale of hundreds to thousands of years.

There are several microbially "pathways" to form humic substances:

- degradation and abiotic condensation;
- degradation of primary resources and resynthesis;
- selective preservation from plant lignins and tannins;
- direct participation in humic substances production and degradation via enzymatic activities.

Humic substances can be:

1. humic acid;
2. fulvic acid
3. humin.

The humic acid contains ≈ 10% more C, but 36% less O than fulvic acid; there are smaller differences in H, N and S content.

The final phase of humification is direct genesis or degradation of humic substances.

During mineralization, organic N is hydrolyzed to release NH_3, which become the cation NH_4^+, as ammonification.

$OrganicN(R-NH_2) \rightarrow NH_3 \rightarrow NH_4^+$ (bind with clays in soil)

Nitrification

Nitrification is an aerobic process, autotrophic and heterothrophic.

Autotrophic nitrification is a two – step process:

- first step, Nitrosomonas:

$$NH_4^+ \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} NH_3 \longrightarrow NO_2^- \longrightarrow NO_3^-$$

- second step, Nitrobacter:

$$H^+ + NO_2^- + H_2O \xrightarrow[\text{dehydrogenase}]{\text{Nitrite}} NO_3^- + 3H^+$$

Autotrophic nitrification is dominant type in agricultural soils.

Heterotrophic nitrification is the oxidation of organic N and NH_3 by Arthrobacter, Streptomyces and Aspergillus, in acid soils

$$R\text{-}NH_2 \longrightarrow RNHOH \longrightarrow \underset{\text{Nitroso-compound}}{(R\text{-}NO)} \longrightarrow R\text{-}NO_3 \longrightarrow NO_3^-$$

In waterlogged environments, denitrification is the major reductive fate of NO_3^-, catalized by distinct enzymes, which produces N oxides such as NO, N_2O and N_2 as a final product.

The major concern with nitrification is the production of NO_3^-, which is readily leached from soil.

Nitrates

Nitrate is a natural product that is always present in soil, cycled very efficiently between soil microbes, soil solution, and plants so the concentration is normally low and losses are small. In order to grow yields of agricultural crops, various practices are adopted and the use of inorganic fertilizers is particularly important (80 million to year^{-1}). The nitrate ion is extremely soluble in water and can easily be washed out of soil to natural waters by leaching and surface runoff. In the EU a limit of 50 mg l^{-1} nitrate (equivalent to 11.3 mg l^{-1} of nitrate - N) has been imposed on any ground – or surface – water to be used as a source of drinking water.

The period immediately after N fertilizer application is a time of high risk of nitrate loss. There are many examples (if high rainfall exists) of much lower recoveries, implying losses of 50% or even more.

It was claimed that NO_3^- from drinking water or vegetables was reduced to NO_2^- by bacteria in the mouth and in the stomach could react with amines to form N – nitrosamines, which are carcinogenic. It can be concluded that there is now no medical evidence to suggest any link between nitrate intake and stomach cancer. [3]

Methemoglobinemia or blue – baby syndrome is a serious disease that can kill infants less than 1 year old. Nitrite can react with hemoglobin and block the site that transports oxygen. The process only occurs when water is contaminated by gastroenteritic bacteria from sewage. Any nitrate escaping to streams, rivers, or lakes can increase the growth of water plants (algae) and thus alter the ecology of aquatic systems.

Cadastral territory Ortișoara

For the main soil types of Romania, Vintila I. (1987) [13] presents the following average values:

- Chernozems Calcic:
  - Humus 3.15%, Nitrogen, total 0.189% - Bărăgan;
  - Humus 3.69%, Nitrogen, total 0.189% - Moldova;
- Chernozems Haplic:
  - Humus 2.94%, N total 0.162% - Bărăgan;
  - Humus 3.57%, N total 0.175% - Moldova;
- Phaeozems:
  - Humus 4.17%, N total 0.218% - Moldova;

Analytical data Timișoara – average values – Table 2

Soil type	Chernozems 17profiles	Phaeozems 6profiles	Cambisols 2profiles	Haplic Luvisols 14profiles
C %	1.87	2.28	1.69	1.69
Humus %	3.21	3.93	2.90	2.91
Total reserve of humus 0-150cm to/ha	183.82	224.85	133.30	168.10
Nitrogen % (total)	0.143	0.165	0.140	0.133
NO_3 ppm, 0-30 cm	31.2	22.8	8.5	8.8
C/N	13.05	13.82	12.07	12.72

Soil type	Albic Luvisols Stagnic Luvisols 6 profiles	Vertisols 2 profiles	Pellosols 9 profiles
C %	1.35	2.29	1.96
Humus %	2.32	3.94	3.37
Total reserve of humus 0-150cm to/ha	156.53	189.34	176.68
Nitrogen % (total)	0.108	0.152	0.141
NO_3 ppm, 0-30 cm	7.8	34.8	32.1
C/N	12.50	15.07	13.90

Soil type	Gleysols 2 profiles	Solonetz 1 profile	Anthrosols eroded phases 3 profiles
C %	1.91	1.69	1.42
Humus %	3.29	2.91	2.44
Total reserve of humus 0-150cm to/ha	195.3	153.14	101.43
Nitrogen % (total)	0.128	0.154	0.108
NO_3 ppm, 0-30 cm	6.8	38.4	4.3
C/N	14.94	10.99	13.13

In soils, N is present predominantly in organic form, and inorganic N is made available by the mineralization of organic N to NH_4^+ and subsequent oxidation to NO_3^-. Plants in soil will preferentially assimilate $NO_3^- \rightarrow NO_2^- \rightarrow NH_4^+ \rightarrow N_2$. When the C/N ratio exceeds approximately 25, net immobilization of inorganic N from soil occurs and, there is insufficient N to sustain microbial activity. The C/N ratio determines the rates at which N (and C) are released and mineral N made available for plant uptake.

All the soil types analysed have a C/N ratio under value 25, the range is between 10.99 (Solonetz) and 15.07 (Vertisols).

The greatest values for Humus and N content are in the Phaeozems (3.93% Humus, 0.165% N), Vertisols (3.94% Humus, 0.152 % N) and Chernozems (3.21% Humus, 0.143 % N).

Since plants uptakes preferentially NO_3^-, it can be seen that Chernozems and Phaeozems have a great content of NO_3^- (22.8 – 31.2 ppm) and, sure with the greatest fertility. [5]

An apart situation is in the case of Vertisols (and Pellosols), which has 3.94 % Humus (and 3.37% Humus), with 34.8 ppm NO_3^- (32.1 ppm). Vertisols are deep clayey soils (>45% clay) dominated by clay minerals such as smectites, with low hydraulic conductivity and stickiness when wet. It is assumed that N, NO_3^- and Humus are strongly adsorbed on external and internal surfaces of smectites and so retains its very strong. Vertisols are rich chemically but only as reserve.

Management practices for crop production ought to be primarily directed to control water dynamics. [8]

The nitric horizon associated with humus – rich surface horizons and saline subsoils is characteristic for Solonetz. Natric horizon has a great clay content and a high amount of exchangeable sodium (30-50 %) and a pH 9-10. [12]

4. CONCLUSIONS

In soils, N is present predominantly in organic form, and inorganic N is made available by the mineralization of organic N to NH_4^+ and subsequent oxidation to NO_3^-.

When the C/N ratio exceeds approximately 25, net immobilization of inorganic N from soil occurs and, there is insufficient N to sustain microbial activity. The C/N ratio determines the rates at which N (and C) are released and mineral N made available for plant uptake.

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REFERENCES

[1]*T.C Balser,* Humification, 2005, Encyclopedia of Environments, Elsevier

[2]*N Batjes,* Total carbon and nitrogen in the soils of the world, 1996, European Journal of Soil Science

[3]*N. Benjamin,* Nitrates in the human diet – good or bad, 2000, Annales de Zootechnologie 49

[4]*K.M. Halder, G. Guggenberger,* Organic matter. Genesis and formation, 2005, Enciclopedia of Environments, vol.2, Elsevier

[5]*A. Hodge,* Nitrogen in soils. Plants uptake, 2005, University of York, U.K., Elsevier

[6]*D.S. Powlson,* Understanding the soil nitrogen cycle, 1993, Soil use and management 9

[7]*Gh. Rogobete,* Stiința Solului, 1994, Editura Mirton, Timisoara

[8]*Gh. Rogobete, D. Țărău,* Solurile și ameliorarea lor, 1997, Edit. Marineasa, Timişoara

[9] *J.I.. Sprent,* Symbiotic fixation, 2005, U.K, Elsevier;

[10] *F.J. Stevenson and M.A Cole,* Cycles of Soils, 1999, New York, John Wiley

[11]*E. Stoica, C. Răuță, N. Florea,* Metode de analiză chimică a solului, 1986, ASAS, București

[12]*V. Tudor, Gh. Rogobete, C. Tudor, A. Bandu,* Considerations about the humus and nitrogen content in the Low Plain Timiş - Bega, Intern.Symposion, USAMVB, Timişoara

[13]*I. Vintilă, Z. Borlan, C. Răuță, D. Daniliuc, L. Țigănaș,* Situația agrochimică a solurilor din România, 1984, Edit. Ceres, București