SOURCES OF EUTROPHICATION OF THE WATERS IN CALARASI

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COUNTY

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#### Abstract

This paper aims to study the factors leading to eutrophication in Calarasi county and then in the Danube, due to the fact that this county has many cultivated areas. In this regard, many factors that lead to nitrate pollution, especially from agricultural sources have been taken into account. In order to model soil nitrate nitrogen in Calarasi county, which can be partially used by plants or leached, researches on soil with the largest share of the county, a chernozem, were made. This study tried to model in the laboratory the influence of three factors on which groundwater pollution by nitric oxide depends: soil type, environmental conditions (temperature and humidity) and the amount of mineral fertilizers incorporated. The amount of nitrate increased with dose of nitrogen fertilizer, the maximum temperature was  $20^{\circ}C$  and was favourably influenced by humidity of 70-80% of field capacity.

Key words: eutrophication, nitric chernozem, pollution

## INTRODUCTION

Current agricultural practices threaten present and future water reserves in Europe.

Inorganic fertilizers are commonly used in agriculture to achieve higher yields. Most fertilizers are composed of three elements: nitrogen, phosphorus and potassium. The most common are fertilizers containing nitrogen and nitrates. This nitrogen is absorbed by plants, it is a very important nutrient. But plants can not consume all the nitrogen spread on the field so much is washed by rain, reaching lakes, rivers or canals which causes eutrophication. Another quantity of nitrogen enters the soil, being driven into the ground water coming from rain or irrigation. There, nitrogen mixes with water in porous rocks - groundwater - where it can remain for a long time – for years.

Eutrophication affects all categories of aquatic ecosystems, but manifests mainly in stagnant ecosystems. The degree of eutrophication of aquatic ecosystems is expressed mainly by the concentration of nutrients (total nitrogen and total phosphorus), oxygen saturation and phytoplankton biomass. Nitrogen is the mineral element, essential to plants, it causing crop yields. Mineral fertilizers have risen over time problems, especially the processes of mineralization and nitrification of nitrogen from the soil.

Given that soil organic matter can provide the plants through mineralization processes large amounts of nitrogen, it is required increasingly further research on finding ways to optimize nitrogen regime to ensure efficiency of mineral fertilization [3].

Nitrogen fertilization is very important now, when agriculture is subject to requirements to raise crop yields, which requires optimal nitrogen supply and the need to protect the environment, caused by involvement mineral nitrogen to groundwater. For these reasons, it requires a very precise quantification of soil nitrogen mineralization.

Establishing adequate quantities of nitrogen as fertilizer for different crops is a very difficult operation because of the many factors to be taken into account, the most important being nitrogen needs of crops and the quantities of nitrogen assimilated by soil redundant cycle vegetation.

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Transformation of nitrogen fertilizers, nitrogen passing from one form to another can result in chemical often assimilable mineral nitrogen loss and changes in soil reaction, which would reduce the effectiveness of fertilizers.

Nitrogen fertilizers were used in increasingly larger quantities in order to increase production, but they led in time to the increase of the amount of nitrate in ground water in agricultural and default.

These nitrates leaching into groundwater and pollute. About 75% of EU residents depend on water tables for their water supply.

Under the Black Sea Environment Programme (BSEP), studies were developed that revealed that 58% of the total nitrogen and 66% of the total phosphorus in waters reaching the Black Sea from the Danube basin (50% in agriculture, about 25% of household activities and only 10-13% of industrial activities) [3].

Over 50% of the volume of nitrogen entering the Danube in the territory of many countries is due to agriculture. Romania is quantitatively the most important source, because its waters on the entire territory drain into the Black Sea.

Nitrogen mineralization is a key issue for all soils and all geographies. But for Calarasi county, it has great importance because it contributes decisively to the production of grains in Romania and soils of this county contributes greatly to cover crop nitrogen requirements for training. On the other hand, excess nitrate in soil is leached in depth, contaminating groundwater and, in many ways, is transported to surface waters and eventually into the Danube. However, Calarasi county is in the end of the great river, near areas critical to fisheries and tourism in Romania. The county is bordered on its eastern side by Borcea Pond, a little north is the Big Island of Braila and finally the Danube Delta.

All these considerations calls for very rational knowledge and management in soil mineral nitrogen production Calarasi: should occur as mineral nitrogen as needed for agricultural production, but should be avoided which causes excess nitrate contamination of ground and surface water. In order to solve this complicated problem - both in Romania and in other European Union countries - stringent rules were imposed on periods of fertilization of different cultures and establishing rational doses of fertilizers.

Since 1999. the Romanian Government adopted a national action plan for environmental protection (NEAP). А component of NEAP is to identify ways to reduce leakage nutrients (nitrogen and phosphorus) into the Danube and the Black Sea and enforce the provisions Nitrates Directive (Council Directive 91/676 / EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources).

The basic principle in resolving disputes arising from pollution is that the polluter pays. As a result, the EU has established strict rules requiring compensation for farmers who do not comply humus mineralization of land they manage and farmers not properly managed composting and waste management resulting from their work.

Problem organic nitrogen mineralization correspondence between intensity and time when it is necessary plant nutrition is of great importance in agriculture. It is known that the activity of micro organisms capable of decomposing organic matter of the soil is usually highest during the crop plants do not exhibits its maximum absorption. Therefore, soil can release large amounts of nitric oxide, which in terms of rainfall can easily be trained with soil depth water [3].

## MATERIALS AND METHODS

Pollution sources of mineral waters containing nitrogen (ammonium salts, nitrites, nitrates) are:

- humic substances of which is mineralized annually about 90 kg N active substance and of which up to 30 kg can be leachate to groundwater;

- mineral fertilizers with nitrogen, using a small extent in our country, but that point can be a source of pollution;

- organic substances - animal waste, municipal and communal - which by their

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mismanagement of mineralization, is in fact the main source of pollution of nitrogen mineral compounds.

Nitrogen pollution of groundwater nitrates from the soil depends on many factors [3]:

**1.** Soil type. In Calarasi county there are two types of soil: 80% of the agricultural area is covered with chernozem and 20% the alluvial soil in the Danube Meadow.

2. *Environmental conditions.* As any biological process, nitrification is influenced by climatic conditions: temperature and humidity.

3. The amount of mineral fertilizers. Production of nitrates in the soil depends on the amount of mineral fertilizers incorporated.

Nitrate content best reflects the momentary conditions to ensure nitrogen plants cultivated soils.

Nitrates are the only natural source of nitrogen available for relatively neutral pH soils in Calarasi county. In optimal conditions for nitrifying flora, ammonia nitrogen from mineral and organic fertilizers into the soil is rapidly converted to nitrate.

To model soil nitrate nitrogen in Calarasi county, which can be partially used by plants or leached, researches were made on soil samples collected from Amp horizon (0-20 cm) in three repetitions field and were mixed into a composite sample of experimental variant.

The soil studied is a cambic chernozem soil with good fertility: humus in soil from 2.6 to 2.9% 2.9 to 3.1% in irrigated and nonirrigated soil, total nitrogen 0.11 to 0.12%. Soil reaction is characterized by a neutral pH (6.3 to 7), with small differences in the profile. Buffering capacity of the soil is good. Dose of nitrogen fertilizer NH<sub>4</sub>NO<sub>3</sub> (N active substance) had graduations: N<sub>0</sub>, N<sub>60</sub>, N<sub>120</sub>, N<sub>160</sub>, N<sub>240</sub>.

Samples were processed at three extreme regimes of temperature  $(5^{\circ}C, 20^{\circ}C, 30^{\circ}C)$  and humidity (40%, 80%, 100% of field capacity) for a better modelling of the nitrification process.

From soil samples subject to conditions above and incubated for 15 days, the amount of nitric spectrophotometer method was determined. [5]. Nitrate extraction was done with a solution of  $K_2SO_4$ . Nitrate dosing was phenol-disulphuric acid, by which nitrates are bound to nitro-acid phenol-disulphuric, coloured in yellow in alkaline medium. Colour intensity obtained depended on the concentration of nitrates. Extinction maximum was at 410 nm.

 $HNO_3 + C_6H_3$  (OH)  $(HSO_3)_2 = C_6H_2$  (OH)  $(HSO_3)_2$  (NO<sub>2</sub>) + H<sub>2</sub>O

 $C_6H_2$  (OH) (HSO<sub>3</sub>)<sub>2</sub> (NO<sub>2</sub>) + 3NaOH =  $C_6H_2$ (ONa) (NaSO<sub>3</sub>)<sub>2</sub> (NO<sub>2</sub>) + 3H<sub>2</sub>O

(alkali salt of the acid 6-nitrophenol - 2.4 disulphuric yellow)

Content expressed in ppm nitrate N in soil was calculated using the formula:

N (ppm) = 
$$\frac{C \times V_e}{m \times a_e}$$

where:

C = N content of the sample, in micrograms;

 $V_e$  = volume in ml of extract soil;

m = mass of soil taken into consideration, in g;

 $a_e$  = volume of aliquot part of the extract, in ml.

### **RESULTS AND DISCUSSIONS**

The results obtained from the analyzes are presented in tables and figures below:

Table 1. Influence of incubation temperature  $(5^{\circ}C)$  the soil samples according to moisture and chemical fertilizers with nitrogen on nitrification potential.

Temp.	C.C.A.	Dose	NO <sub>3</sub> (ppm)	
(°C)	(%)	nitrogen (Nkg/ha)	Initial	Final
		0	1,79	0,56
		60	1,98	0,70
	40%	120	1,74	0,76
		160	2,68	1,08
		240	2,13	1,46
		0	1,79	0,45
		60	1,98	0,86
5°C	80%	120	1,74	1,22
		160	2,68	1,26
		240	2,13	1,64
		0	1,79	4,46
		60	1,98	4,55
	100%	120	1,74	5,93
		160	2,68	5,52
		240	2,13	5,54

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Table 2. Influence of incubation temperature (20°C) the soil samples according to moisture and chemical fertilizers with nitrogen on nitrification potential.

Temp.	C.C.A.	Dose	NO <sub>3</sub> (ppm)	
(°C)	(%)	nitrogen (Nkg/ha)	Initial	Final
20°C	40%	0	1,79	2,85
		60	1,98	3,50
		120	1,74	2,85
		160	2,68	3,39
		240	2,13	3,80
	80%	0	1,79	2,88
		60	1,98	4,21
		120	1,74	4,39
		160	2,68	8,24
		240	2,13	5,92
	100%	0	1,79	5,96
		60	1,98	6,65
		120	1,74	7,21
		160	2,68	6,54
		240	2,13	7,09

Table 3. Influence of incubation temperature (30°C) the soil samples according to moisture and chemical fertilizers with nitrogen on nitrification potential.

Temp.	C.C.A.	Dose	NO <sub>3</sub> (ppm)	
(°C)	(%)	nitrogen	Initial	Final
		(Nkg/ha)		
	40%	0	1,79	3,48
		60	1,98	4,76
		120	1,74	4,92
		160	2,68	5,99
		240	2,13	3,90
	80%	0	1,79	3,48
		60	1,98	5,08
30°C		120	1,74	6,02
		160	2,68	7,75
		240	2,13	7,10
	100%	0	1,79	3,38
		60	1,98	4,52
		120	1,74	5,33
		160	2,68	5,74
		240	2,13	7,19

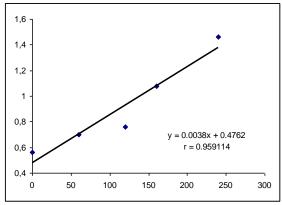
Regarding the nitrification process depending on the moisture-aeration of the soil during incubation of soil samples - there is a clear increase from 40% to 100% of field water capacity.

Nitrogen fertilization increases mineralization. Also, nitrogen mineralization increases once with the temperature. However, the incubation temperature of  $30^{\circ}C$ and field capacity water 100% mineralization intensity decreases, probably due to exacerbated de-nitrification.

At  $30^{\circ}$ C, mineralization, nitrification capacity is much higher than that at  $5^{\circ}$ C.

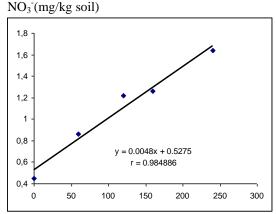
This is probably because the  $5^{\circ}$ C biological processes are slowed down and that the real changes occur at  $30^{\circ}$ C, temperature optimum soil life. Between  $20^{\circ}$ C and  $30^{\circ}$ C temperatures, there are no significant differences.

NO<sub>3</sub><sup>-</sup>(mg/kg soil)



Dose of nitrogen fertilizer

Fig.1. Correlation nitrification capacity of nitrogen fertilizer dose in cambic chernozem, at  $5^{0}$ C and 40% field capacity water.



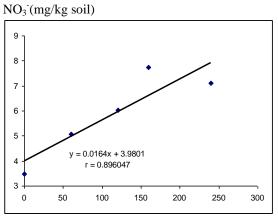
Dose of nitrogen fertilizer

Fig.2. Correlation with nitrification capacity dose of nitrogen fertilizer on cambic chernozem, at  $5^{0}$ C and 80% field capacity water

In Figures 1 and 2 it is shown that the amount of nitrogen fertilizer positively influenced soil nitrification potential. In both cases, growth is evident. Large correlation coefficients colinearity demonstrates this point.

In Figures 1 to 4 it is observed that the amount of nitrogen fertilizer influenced the nitrification potential.

The amount of nitrate increased with dose of nitrogen fertilizer.



Dose of nitrogen fertilizer

Fig.3. Correlation with nitrification capacity dose of nitrogen fertilizer on cambic n chernozem, at  $30^{\circ}$ C and 80% field capacity water

 $NO_3^{-}(mg/kg \text{ soil})$ 

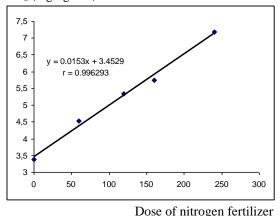


Fig.4. Correlation nitrification capacity of nitrogen fertilizer dose in cambic chernozem at  $30^{\circ}$ C and 100% field capacity water

The correlation is strong, especially at 100% of field water capacity. These findings confirm previous data presented widely by Ghinea and Stefanic [2] and the finding that they actually provide the ability mineralization, nitrification is the most accurate index for assessing crop nitrogen need [1].

We observed that 100% of field capacity for water nitrification process has not varied in intensity depending on the two factors of influence. It may be only discriminating factor insufficient oxygen, knowing that nitrifying bacteria to oxidize ammonia are designed and that its deficiency conditions are limited nitrification process.

County public wells are dug shallow, leading to their contamination with nitrite poisoning risk for occurrence and bacterial diseases. In 2011, in Calarasi county, there were 5 cases of infant acute methemoglobiemia caused by well water [4].

### CONCLUSIONS

The optimum temperature for the activity of nitrifying bacteria is between  $20-30^{\circ}$ C. Also, exerts an important role is the soil moisture on nitrifying bacteria that grows and nitrifies best when soil moisture is between 70-80% of field capacity.

For chernozem soil, mainly in Calarasi county, the optimum temperature for nitrification activity and therefore the highest amount of nitrate was obtained at  $20^{\circ}$ C, regardless of the dose of fertilizer and moisture. At temperatures below  $10^{\circ}$ C a decrease was in the amount of nitrates in the soil as it blocks the transformation of ammonia into nitrates.

It was found that humidity affects differently the nitrification process. Humidity between 40-80% of field capacity influences the most the nitrates amount, as the optimum conditions for aeration and moisture are met, condition needed for this process.

The use of mineral fertilizers in increasing doses influences the nitrate accumulation in soil. Highest amounts of nitrate were obtained at doses ranging from 150-200 kg nitrogen per hectare  $NH_4NO_3$ .

For the pollution prevention and control of the mineral nitrogen, both at European and national level, directives were adopted, that consider the orientation towards sustainable agriculture and a national code of good agricultural practice, compulsory for all Romanian farmers.

To avoid pollution by nitrogen minerals, adopting a rural development plan, including measures of water supply, sewerage all localities and wastewater remediation and livestock waste is the most important measure.

Mineralization of organic matter and nitrates washing phenomena are strongly influenced by use of soil and crop technologies.

Both economically and in terms of protecting the environment, it is necessary to reduce this

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loss, which is possible by adopting proper agricultural practices.

Nitrate losses from the soil are more intense in seasons of abundant precipitation, when usually the soil is devoid of vegetation. In specific conditions of Calarasi county, after annual crops, in the soil remain higher or lower amounts of mineral nitrogen fertilization coming from above (about 50% of the nitrogen applied to crops remains unused) and mineralization of soil organic matter.

Mineralization is most intense in autumn (when they meet favourable conditions of temperature and humidity) and there is also an increased risk of water pollution by nitrates. In countering this phenomenon, crop rotation is essential. It is good to be interspersed with the main crop in a crop rotation with rapid growth, able to capitalize residual nitrogen in the spring and it can be used in spring as green manure for spring-summer crops.

In order to reduce nitrogen losses and the risk of pollution of the Danube water, it is good to choose appropriate rotations, ensuring soil covered with vegetation maintenance for a longer period of time, especially in wet seasons, to manage crop residues as fairly (especially where the C/N ratio is high) and is limited to the minimum necessary ground work on mobilization.

Other means of reducing residual nitrogen can be: rotation that also includes a winter crop, intercrop introduction of native species, resistant to cold and frost quickly able to occupy the land and form a vegetation cover often enough and uniform to protect the soil from rainfall effect autumn - winter.

The European Union policy and legislation in the field of pollution in agriculture should be considered in assessing the legal framework for pollution control in agriculture. According to this policy, the agricultural practices defined in the "Code of Good Agricultural Practice" constitute minimum environmental standards to which farmers can be called to join, without the right to compensation.

Regulatory solution to control the diffuse pollution in the agriculture of Calarasi county should be directed towards finding solutions that meet current reality in our country and contribute to the effective fulfilment of Romania obligations resulted from the international legislation.

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