# SOIL POLLUTION WITH CHEMICAL FERTILIZERS

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***Abstract:*** *The paper presents general aspects regarding the importance of chemical fertilizers for agriculture and for the development of the economy, their classification and agrochemical aspects. The stages of nitrogen transformation in soil are: fixation, assimilation, ammonification, nitrification and denitrification. Chemistry of agriculture through the uncontrolled and inappropriate use of chemical fertilizers correlates with environmental problems and the soil is subject to a complex impact.*

***Key words:*** *pollution, soil, fertilizers, chemistry*

## 1. Introduction

The use of chemical fertilizers = ***chemistry*** in agriculture and forestry has been a synonymous formula with progress and development, since chemistry, mechanization, irrigation, modern agrotechnics have contributed to the substantial increase of agricultural, fruit, wine and forest products.

The positive effect of agriculture is due to green plants, which, by absorbing CO2 from the atmosphere for its use in photosynthesis and O2 removal, purifies the air. Pollutants such as volatile substances, CO2, SO2 and NH3, can be directly absorbed by green plants, with an atmosphere of purification. In the soil, excess nitrogen is leached in the form of nitrates into the groundwater and then into drinking water. Increasing the water content in phosphorus stimulates the growth of algae and other aquatic vegetal organisms. The intensive use of fertilizers with nitrogen, phosphorus and potassium leads to the increase of soil content in Zn, Pb, Ni, Cr, which were in soluble forms, only as traces.

After 1955, with the industrialization and development of agriculture, a strong chemical fertilizer industry has developed. In Romania, the consumption of fertilizers increased strongly after 1965, reaching over 1,200,000 t in 1980, ie an average consumption of 120 kg / ha or 60 kg / inhabitant.

The importance of the use of chemical fertilizers has been demonstrated by the fact that plants extract large amounts of nutrients from the soil. In this respect, the chemical fertilizers must contain the main macroelements N, P, K and Ca, Mg, S, as well as Fe, Cu, Zn, B, Al, Mn, Mo, etc. (table 1).

*Table 1. Nutrients present in chemical fertilizers*

| | | | |
|---|---|---|---|
| SUBSTANȚE HRĂNITOARE | AZOT | N | FERTILIZATOR MAJOR |
| | FOSFOR | P | |
| | POTASIU | K | |
| | SULF | S | FERTILIZATOR SECUNDAR |
| | CALCIU | Ca | |
| | MAGNEZIU | Mg | |
| | FIER | Fe | MICROELEMENTE |
| | BOR | B | |
| | MANGAN | Mn | |
| | CUPRU | Cu | |
| | MOLIBDEN | Mo | |
| | COBALT | Co | |
| | ZINC | Zn | |

*The classification of chemical fertilizers* is made according to several criteria:

- ✓ *origin (provenance)*
- organic - natural - from the animal or vegetal environment
- minerals - chemical - artificial - synthesis - coming from the mineral kingdom or chemical - mechanical preparation in the factories
- ✓ *state of aggregation*
- solid

- liquids - apply to foliage at different stages of plant growth

✓ *number of nutrients contained*

- simple - contain only one nourishing element (nitrogen - *ammonium nitrate* or phosphorus - *superphosphate*)
- complex - contain two or more elements (nitrogen and phosphorus – *Nitrofos*; nitrogen, phosphorus and potassium - *Nitrofoska)*

✓ *presentation form*

✓ *nature of nutrients*

- with nitrogen
- with phosphorus
- with potassium
- with microelements

**2. Agrochemical aspects of chemical fertilizers**

***Chemical fertilizers*** are obtained by the physical or chemical processing of products of inorganic nature. In relation to the nutrients they contain as a basic element, they are divided into the following main groups (fig. 1):


*Fig. 1. Types of chemical fertilizers and how they are packaged, stored and presented*

***1).Nitrogen fertilizers***

- are salts of strong acids (H2SO4, HCl), ammonium or nitric acid with different cations (NH4 +, K +, Ca2 +), as well as weak acids (H2CO3, HCN), ammonium or amide radical -NH2
- classification of nitrogen-based fertilizers by composition:

*a. Nitric nitrogen fertilizers*: NaNO3 - 16.4% N and 27% Na; Ca(NO3) 2 - 15.5% N and 36% Ca; KNO3 - 13.7% N and 46.5% K2O

*b. Nitrogen fertilizers in ammoniacal form*: NH3; NH4SO4; NH4Cl

*c. Fertilizers with nitric and ammoniacal nitrogen*: NH4NO3; NH4NO3 x CaCO3; NH4NO3 (NH4) 2SO4

*d. Amide (ureic) nitrogen fertilizers:* CO(NH2)2; CaCH2

*e. Fertilizers with organic nitrogen*

- organomineral type L-200 and L-300 - fertilizers containing organic nitrogen and obtained from lignite (organic nitrogen) and urea (amide nitrogen)

*f. Fertilizers with organic and mineral nitrogen*

- urea addition compounds - besides amidic nitrogen, contain ammoniacal nitrogen (ammonium ureosulfate with 33.7% N) or nitric nitrogen (urea nitrate -34.2% N and calcium ureaazate -34.5% N)

- classification of nitrogen fertilizers by the degree of nitrogen solubility:

- ✓ soluble (most)
- ✓ slightly soluble

- nitrogen deficiency leads to slowing the formation of antidotes and to stopping the growth of leaves and tissues; thus the plants stop growing, the leaves remain small, they get a light green color, they become yellow and fall

***2). Fertilizer with phosphorus***

*a. Simple Superphosphate* - contains 17-19% total $P_2O_5$ and 14-17% water-soluble $P_2O_5$

*b. Concentrated superphosphate* or triple superphosphate - contains 46-47% total $P_2O_5$, 46% $P_2O_5$ soluble in conventional solvents and 44% water-soluble $P_2O_5$

*c. Thomas slag* (basic slag) - a by-product of steel manufacture

*d. Ammonium phosphates* - phosphorus-containing products in the form of highly water-soluble mono- and diammonium phosphates and conventional solvents

*e. Nitrophosphates* - complex fertilizers, obtained by attack of phosphate rock with nitric acid

***3). Potassium fertilizers***

- contain different potassium salts, especially strong acids (HCl, $H_2SO_4$) or weak acids ($H_2CO_3$, $H_4SiO_4$, $H_2SiO_3$, $H_4Al_2Si_2O_9$)
- classification of potassium fertilizers based on solubility and accessibility for plants:
- ✓ *easily soluble in water and easily accessible to plants*
- ✓ *slightly soluble in water*

***4). Fertilizers with secondary macroelements***

*Fertilizer with magnesium*: *Dolomite* $CaCO_3 \times MgCO_3$; *Magnesium sulphate* $MgSO_4 \times 7H_2O$ - White, crystallized, water-soluble salt contains 9.9% Mg.

*Sulfur fertilizers*: *Elemental sulfur; Inoculated sulfur; Gips* $CaSO_4 \times 2H_2O$

***5). Fertilizer with microelements***

Fertilizer with iron

- ✓ *Ferrous sulphate* $FeSO_4 \times 7H_2O$ - light green crystalline salt containing 20.1% Fe. In contact with air, it loses crystallization water, and the bivalent iron passes into trivalent forms.
- ✓ *Chelated by iron* - yellow-brown organo-mineral salts. They can be applied in powdered form or in solution to combat iron deficiencies. They contain an average of 8-12% iron. The most well-known is the sodium and iron salt of ethylene diamine tetraacetic acid (NaFe-EDTA), which is named Commercial *Versena* and Fe-EDDHA called *Sequestrene*. When applied in solutions, concentrations of 5-10 ppm of Fe metal are used. As a powder, apply 10 to 20 g of Fe to a tree.
- ✓ *Ferric ammonium phosphate* $Fe(NH_4)PO_4 \times H_2O$, contains 29% Fe.

***6).Complex and mixed fertilizers***

• classification of complex and mixed fertilizers by composition:

- ✓ two elements, such as: NP, NK, PK, MgN, MgP, MgK
- ✓ three elements, such as NPK or multiple elements
- ✓ various residual products of a mineral or organic nature, with a complex chemical composition, which are used in the form of powders or flours

**3. Soil pollution with chemical fertilizers**

Farming chemistry through the uncontrolled and inappropriate use of chemical fertilizers correlates with the increase of agricultural production, but also with the problems generated by the environment:

- chemical fertilizers lead to depletion of natural soil fertility and an imbalance in the natural soil composition
- N and P chemical fertilizers lead to the dissemination of nitrogen and phosphorus in the environment with unfavorable consequences on surface water eutrophication and biological equilibrium
- chemical fertilizers cause changes in crop quality and elements by accumulation of nitrates, carbohydrates, lipids, change of C / N, N / P and Ca / Mg
- the residual effect of some chemicals in the diet contributes to the promotion of modern diseases
- intensive agriculture changes biocenoses and creates an ecological imbalance

The most polluting effect is the excessive use of nitrogen fertilizers: ammonium nitrate nitrate NH4NO3, calcium nitrate Ca(NO3)2, ammonium sulphate (NH4)2SO4 and urea NH2 - CO - NH2. Ammonium nitrate and urea introduced into the soil, by hydrolysis and by the action of nitrifying bacteria, give rise to nitric (nitrogenous) NO3- ions. Following reactions between HNO3 and HNO2 with soil bases, nitrates (nitrates) and nitrates are formed. Azotates are readily soluble, and in excess they reach the groundwater that they pollute. It turns into the human and animal's digestive tract in the nitrates and favors the conversion of hemoglobin into methemoglobin, preventing oxygenation of the blood. Nitrates turn into nitrosamine, a toxic and carcinogenic product. With chemical fertilizers, Cl (KCl), F-, SO42- (from P fertilizers) come into the soil, but their quantity is small and is not an ecological hazard. Nitrogen fertilizers used in excess have the most polluting effect, and by leaching, excess nitrate enhances the eutrophication process of surface waters. Nitrogen-based chemical fertilizer overdoses alter the bacterial flora in the soil, altering the relationship between the destroyers and other groups of organisms in the agro-system, and eliminating or inhibiting nitrogen-binding bacteria by canceling the regeneration of soil fertility. Overdosing with chemical fertilizers, especially with nitrogen salts, is very dangerous because it contributes to the pollution of soil, ground water and plants (fig. 2).

Phosphorus is dispersed in the form of superphosphates, and potassium in the form of potassium nitrate (KNO3), silvinyl (KCl). Risks of pollution with P and K are low because they are fixed to mineral compounds in the soil. The amount of phosphates circulating between the lithosphere, soils and the hydrosphere has increased considerably. Part of P is immobilized in Ca and Fe soil, and part is entrained by continental waters to water basins or to groundwater, with an inductive role in water eutrophication.

*Fig. 2. Soil pollution by inappropriate application of chemical fertilizers*

In conditions of long-term use and over-fertilization, the soil quality is affected by the macro-elements they contain and by the elements present in the traces. Decreasing the pH of

the soil solution (in the process of assimilation of macronutrients) or the development of certain microorganisms can create conditions for the mobilization of these microelements with the effect of inhibiting the activity of the organisms or bioaccumulation therein.

In order to delimit the vulnerable or potentially vulnerable areas from nitrate pollution caused by the inappropriate use of chemical fertilizers at the level of Gorj county, a methodology was applied based on the analysis of each subsystem (ground, subsoil, groundwater, surface water, plants) from the perspective of the production and transmission of nitrates from agricultural sources, to the soil and by the phenomenon of dispersion and transport, implicitly to the other environmental factors. In applying the methodology, two steps were taken:

- Delimitation of vulnerable areas at the level of administrative territorial units, depending on the type of nitrate sources:
  - current sources: The present agricultural activities produce a surplus of nitrates due to the high animal density
  - historical sources: zootechnical complexes that have been in operation in the past and have been decommissioned
- Consideration of river basins for vulnerable localities

Legislation for areas vulnerable to nitrate pollution presents a limit for organic fertilizer (nitrogen) loads as follows:

- ✓ 250 kg / ha of total N on hayfields
- ✓ 210 kg / ha of total N on arable land

These are average values for the entire agricultural land classified as a vulnerable zone to nitrate pollution. The loading limit for arable land decreases to 170 kg / ha after the first 4 years of application. In fig. 3 are the vulnerable zones of nitrate soil pollution due to the uncontrolled use of chemical fertilizers in the Jiu Hydrological Basin: Gorj county, Băleşti commune, with 5562 ha of agricultural land and 4078 ha of arable land; Dolj county, Ghercești and Isalniţa communes from the plain area with 4596 ha of agricultural land and 4082 ha of arable land, respectively 2114 ha of agricultural land and 1833 ha of arable land; in the Mehedinţi County, the Gârla Mare and Pristol communes in the plain area with 5485 ha of agricultural land and 4783 ha of arable land, respectively 3269 ha of agricultural land and 3958 ha of arable land.

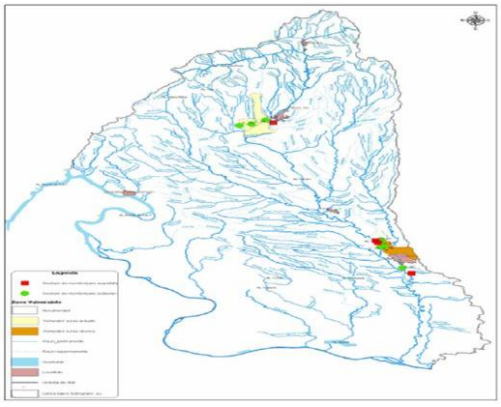

*Fig. 3. Areas vulnerable to soil pollution by nitrates due to uncontrolled use of chemical fertilizers*

In this respect, it is proved that rational fertilization must ensure an acceptable compromise between the necessity to obtain better economic yields of the vegetal production and the protection of the quality of the environment, respectively soil protection, against the pollution with the mineral nutrients from the applied fertilizers. High-tech farming, which preserves and improves soil fertility and productive potential, is able to provide high-class crop systems and protect the quality of the environment.

C**onclusion**

- Chemical fertilizers should contain the main N, P, K, Ca, Mg, S and macroelements Fe, Cu, Zn, B, Al, Mn, Mo.
- The classification of chemical fertilizers is based on several criteria: origin (origin), state of aggregation, number of nutrients contained, presentation form and nature of nutrients
- Chemistry of agriculture through the uncontrolled and inappropriate use of chemical fertilizers is in line with the increase of agricultural production, but also with the problems generated by the environment, especially on the soil.
- In the case of long-term use and over-fertilization, the soil quality is affected by the macro-elements they contain and by the elements present in the traces.

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