BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI Publicat de Universitatea Tehnică "Gheorghe Asachi" din Iași Volumul 64 (68), Numărul 1, 2018 Secția CHIMIE și INGINERIE CHIMICĂ

CHANGES IN SOIL pH DUE TO THE USE OF CHEMICAL FERTILIZERS

ΒY

RAMONA-ELENA TĂTARU-FĂRMUȘ, ROXANA GEORGIANA COCEA, ANCA ADOMNICĂ and NICOLAE APOSTOLESCU*

"Gheorghe Asachi" Technical University of Iaşi, Romania, "Cristofor Simionescu" Faculty of Chemical Engineering and Environmental Protection

Received: February 20, 2018 Accepted for publication: March 24, 2018

Abstract. Although soil is commonly referred to as "fertile substrate", not all soils are favorable for crop cultivation. Soils ideal for agriculture are balanced in terms of mineral, organic, air and water. Each of these factors plays a direct role in obtaining a good quality soil for agriculture. Soil pH is a very important element to be known because it occurs in many physicochemical and biological soil mechanisms. Optimal soil pH range for plant growth varies from one crop to another. Generally, soil pH 6.0-7.5 is acceptable for most plants like most nutrients are available in this pH range. The use of mineral fertilizers, although beneficial and imperative to obtain good qualitative and quantitative crops, changes the soil pH. The present paper proposes a laboratory study on changes in pH caused by the use of mineral fertilizers such as urea, ammonium nitrate, NPK complex fertilizer, combinations of these, with or without the addition of calcium carbonate - as an amendment. The research has revealed the direct link between the use of fertilizers and the modification of soil pH values.

Keywords: chemical fertilizers; NPK; soil pH; urea.

^{*}Corresponding author; e-mail: napostol@ch.tuiasi.ro

1. Introduction

Soil is the most recent natural formation on the surface of the lithosphere, which can be characterized as a material with substantial solid content of variable thickness and represents the upper shell of the crust. Water, air, solid particles, organic and inorganic substances make the soil a real plant capable of creating life and new organic matter. That is why any negative change that occurs in soil functioning is likely to produce negative effects on a whole complex of factors and elements that make up the soil. The chemical composition of the mineral component varies from one soil to another depending on the rocks of origin, soil type, age, vegetation, climate, crop technology (irrigated or non-irrigated, grained, ungrounded) (Brady and Weil, 2008).

Soil pH is a very important element to be known and supervised because it occurs in many physicochemical and biological soil mechanisms. Because the soil also contains water, it has been divided by the pH value into three major categories: acid, neutral and alkaline. Of course, it's an organic matter and we will not encounter soils with pH in one extreme or another than in the case of strong sources of pollution. The soils may have a variable pH between 3.5 and 11.0, but the plants grow normally and well only in the pH range of 5.0-8.5 (Tan, 1993; Davidescu et al., 1981). Knowledge of pH is particularly important because it is determinant in the availability of soil nutrients required for plant cultivation. The basic elements for a balanced soil, which decisively influence the development of the plants N, P, K (nitrogen, phosphorus and potassium), are assimilated to them according to the pH values as follows: nitrogen is assimilated to pH 6-8.5, phosphorus at pH 6.5-8 and potassium at pH> 6. Other elements are assimilated to the following soil pHs: sulfur pH> 6, calcium and magnesium pH 6.5-8.5, iron pH < 6.5, manganese pH 4.5-6.5, pH 5-7, copper and zinc pH 5-7 (Mengel and Kirby, 2001; Avarvarei et al., 1997; Scientific Staff of the International Plant Nutrition Institute, 2010).

Soil pH can also influence the plant growth by its effect on the activity of beneficial bacteria, microorganisms that decompose soil organic matter are hindered in strong acidic soils. Microorganisms involved in nitrification processes need a certain pH of the soil to function efficiently. Since these organisms require large amounts of calcium to make a transformation, a pH of 5.5 to 6.5 is required for calcium ion to be accessible. Also, Rhizobia's bacterial activity, which is responsible for nitrogen fixation in vegetable crops, decreases when the pH drops below 6.0. The processes of decomposition and humification of organic matter that are still under the action of microorganisms are affected by acidic soils (Ghinea, 1985).

Therefore, in order for the soils to maintain their structural characteristics and the ability to support the growth of the plants, their acidity must be avoided. A neutral or slightly acidic soil with a pH range of 5.5-6.5 is ideal for plant growth. At this level of acidity there is a sufficient amount of

calcium ions to support the aggregation of clay and to counteract the effect of acidity. Sources of acidification in the soil are natural (climate, vegetation, rock) or generated by human interference (pollution, fertilizers, pesticides). The use of fertilizers is necessary for long-term production in order to obtain yields that make the harvesting effort useful. Modern fertilizer practices introduced more than a century ago and based on the chemical concept of plant nutrition have greatly contributed to the immense increase in agricultural production and have resulted in improved food and feed quality. As a benefit to the side effects, soil fertility has been improved, resulting in a more stable production level, as well as better resistance to certain diseases and climatic stress.

The pH of the soil is easily determined. The most accurate method of determining the pH of the soil is a pH meter. A second method, which is simple and easy but less precise, is the use of certain indicators or dyes. Using a pH -meter is possible to measure the pH in days when the soil is wet and it is good to do this in several places in the garden to find out more real value. Majority of dyes change their color with an increase or decrease of pH making it possible to estimate soil pH. In making a pH determination on soil, the sample is saturated with the dye for a few minutes and the color observed. This method is accurate enough. There are also natural indicators. The presence of dandelion (Taraxacum officinalis), nettle (Urtica dioica) and wild sorrel (Rumex acetosa) show that the soil is acidic and the growth of plants such as Lepidium campestre, Anagallis arvensis, Silene dioica and Datura stramonium indicate an alkaline soil.

From the point of view of the chemical engineer, the most important classification criteria for mineral fertilizers are: the number and nature of indispensable essential macroelements, the agrotechnical role, the physical state in which fertilizers are delivered, the solubility, the rate of assimilation of nutrients, the physiological reaction of fertilizers (due to the fact that plants selectively absorb nutrients from the soil in the form of ions, the anion being absorbed in excess of the cation and vice versa). Practically, the collaboration between the agronomist engineer (the one who uses it) and the chemical engineer (who produces fertilizers) is absolutely necessary. To show the changes of pH value in soil due to the use of fertilizers, the following fertilizer solutions were prepared: urea, ammonium nitrate, NPK 15-15-15, NPK + Mg + microelements (Tătaru Fărmuş *et al.*, 2017).

Nitrogen (N) is the most important and is applied in the highest doses because it directly determines the harvest mass. It is a plastic substance in the sense that it is in the dry substance composition of the plant. Without nitrogen, there can be no protoplasm and therefore no life. The physiological action of nitrogen is closely related to the phases of vegetation, the water need, and the presence of other nutrients (phosphorus, potassium, etc.). Nitrogen deficiency leads to the slowing of the formation of antidotes, to the reduction or even to stopping the growth of leaves and tissues (Davidescu *et al.*, 1976; Hofman and Van Cleemput, 2004).

2. Experimental

Materials

As fertilizer were tested several combinations containing urea, ammonium nitrate, NPK and NPK-Mg and CaCO₃.

Urea – abbreviated U – with the formula CON_2H_4 , molar mass 60.06 g/mol, is a prilled fertilizer used for almost all crops and soils. By incorporating urea into the soil, ammonia losses are reduced. Urea has a high nitrogen content of 46% N and is therefore very effective. Used correctly, this is a cost-effective and cheap nitrogen source.

Ammonium nitrate – abbreviated AN – with the formula NH_4NO_3 , molar mass 80.043 g/mol is, under ordinary conditions, a white crystalline substance with 60% O, 5% H and 35% N. Ammonium nitrate is a nitrogenous fertilizer representing more than 10% of total nitrogen consumption worldwide. It is more readily available to crops than urea.

Compound fertilizers are the most demanded in agriculture, occupying the first place in terms of quality and quantities of mineral fertilizers manufactured by the chemical industry. Besides having a content with different ratios of the main nutrients (N - P_2O_5 - K_2O), they contain certain secondary and micronutrient agents specific to crop needs in a particular agro - climatic region.

In this paper was used an NPK assortment, type 15-15-15, but also an assortment of type NPK + Mg, 4-12-5 +10 with micronutrients (Cu, Fe, Mn, Mo, Zn). Magnesium (Mg) is a component of chlorophyll, thus participating in the photosynthesis process, but it is also found in other compounds of plant organisms (phytin, pectic substances). As a result, this element is required for both chlorophyll and non chlorophyll plants (fungi, bacteria) (Tătaru Fărmuş *et al.*, 2017; Davidescu *et al.*, 1976).

One of the biggest problems of agriculture is the quality of soils, and here we refer to their acidity due primarily to the excessive use of fertilizers and other chemical solutions that have the effect of lowering the pH. One of the most common solutions for acid soils is calcium carbonate, a white powder with the chemical formula $CaCO_3$.

The pH Experiments

There were prepared seven different fertilizer solutions with 5% mass concentration. Two solutions have been prepared with 5% urea and 5% NPK with the addition of 1% calcium carbonate and another solution of 5% urea - 5% ammonium nitrate. For each of the prepared solutions, the pH was measured with HANNA HI2210 instrument. The recorded values are shown in the Table 1.

Table 1 The pH Values for the Solutions of Fertilizers												
Solutions	U	AN	NPK	NPK-Mg	NPK+CaCO ₃	U+CaCO ₃	U+AN					
pH value	8.7	7.1	4.5	3.9	7.1	9.7	7.1					

To study the changes due to fertilizers, a commercial garden land was used, with a pH value declared on the packaging of this type of land of 6.5. A suspension of 10 g of soil and 100 mL of distilled water (pH = 5.8) was prepared. The suspension was filtered and the pH of the filtrate obtained was measured. The registered value of pH in the laboratory was 7.2.

Under the same conditions of temperature and humidity, weighing 100 grams of soil and weighed in 9 identical, individual boxes (Fig. 1). 7 boxes were designed for fertilizer solutions, 2 were for control samples, soil without fertilizer.



Fig. 1 - Individual boxes with soil for experiments.

Each soil box was hydrated with 60 mL of liquid, obtained from 10 mL of fertilizer solution and 50 mL of water. After 48 h, we measured the soil pH "fed" with this fertilizer solution. Each soil box was hydrated with 60 mL of liquid, obtained from 10 mL of fertilizer solution and 50 mL of water. After 48 hours, we measured the pH of the soil "fed" with this fertilizer solution. The soil was again hydrated with fertilizer solution (60 mL) and after another 48 h, we measured the pH of the soil. The recorded values are shown in the Table 2.

1		1.00	pri va	mes jet n	10 5011 50	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,				
рН	Solutions									
	U	U+AN	AN	NPK	NPK- Mg	NPK+ CaCO ₃	U+ CaCO ₃	Soil		
After 48 h	9.1	8.4	7.5	6,6	6.6	6.9	9.1	7.1		
After 96 h	9.1	8.4	8.0	6,5	6.6	6.8	9.0	7.2		

Table 2The pH Values for the Soil Solutions

Simultaneously with the previous determinations, in twin individual houses with the ones described above (100 g of soil, hydrated with 60 mL of fertilizer solution), we put on 15 wheat grains. The goal was to observe seed yield, depending on the type of fertilizer used and the changes it produces on soil pH.

Discussions

The use of fertilizers such as urea, ammonium nitrate and their combinations led to an increase in the pH of the soil (Fig. 2). The maximum value in the alkaline range was 9.1, in case of fertilized soil with urea / urea and calcium carbonate, measured 48 h after the fertilizer was introduced into the soil.



Fig. 2 – The pH variation depending on the fertilizer type.

The use of NPK complex fertilizers determined soil acidification, more pronounced in the case of NPK 15-15-15 fertilizer, more easily noticeable for the fertilizer solution NPK + $CaCO_3$.



Day 3 Day 6 Fig. 3 – Germination of wheat seeds depending on the fertilizer used.

In terms of wheat grain germination and sprouting, better results have been obtained in the case of soil pH with values between 5.5 and 6.8, corresponding to NPK fertilized soil or combinations thereof (Fig. 3).

3. Conclusions

The soil pH is a very important element to be known and supervised because it occurs in many physicochemical and biological soil mechanisms. The research has revealed the direct link between the use of fertilizers and the modification of soil agrochemical properties. For agriculture, one of the most important soil parameters directly influenced by the use of chemical fertilizers is the pH, which must be continuously monitored and maintained between certain values. Changing the pH determines radical changes in the nutrition regime of crop plants, with direct consequences on yields per hectare and on the quality of production.

The correct choice of the fertilizer type used and the optimization of the applied doses are basic considerations in establishing the fertilization plan in an agricultural holding, thus achieving both the economic efficiency of the activities and the scientific substantiation of the applied technologies.

REFERENCES

- Avarvarei I., Goian M., Davidescu V., Mocanu R., Caramete C., Rusu M., *Agrochimie*, Ed. Sitech, Craiova, 1997.
- Brady N.C., Weil R.R., *The Nature and Properties of Soil*, 14th Ed. Upper Saddle River, NJ: Prentice Hall, 2008.
- Davidescu D., Calancea L., Davidescu V., Lixandru Gh., Agrochimia, Ed. Didactică și Pedagogică, București, 1981.
- Davidescu D., Calancea L., Davidescu V., Handra M., Petrescu O., Azotul în agricultură, Ed. Academiei Republicii Socialiste România, București, 1976.
- Hofman G., Van Cleemput O., *Soil and Plant Nitrogen*, International Fertilizer Industry Association Paris, September 2004.
- Ghinea L., Viața în sol, Ed. Ceres, București, 1985.
- Mengel K., Kirby A., *Principles of Plant Nutrition*, 5th Ed. Kluwer, Dordrecht, Netherlands, 2001.
- Tan K.H., Principles of Soil Chemistry, Marcel Dekker Inc., USA, 1993.
- Tătaru-Fărmuş R.-E., Harja M., Lazăr L., Apostolescu N., Ingineria produselor fertilizante anorganice: Îndrumar de laborator, Ed. Ecozone Iași, 2017, ISBN 978-606-8625-13-3.
- *** Soil pH and the Availability of Plant Nutrients, from Scientific Staff of the International Plant Nutrition Institute (IPNI), 2010.

MODIFICĂRI INDUSE ÎN pH-UL SOLULUI DATORITĂ UTILIZĂRII ÎNGRĂȘĂMINTELOR CHIMICE

(Rezumat)

Deși solul este denumit în mod obișnuit "substratul fertil", nu toate solurile sunt favorabile agriculturii. Solurile ideale pentru agricultură sunt echilibrate în ceea ce privește componenta minerală, componenta organică, aerul și apa. Fiecare dintre acești factori joacă un rol direct în obținerea unui teren de bună calitate pentru agricultură.

Un element foarte important pentru a fi cunoscut este pH-ul solului deoarece apare în multe mecanisme fizico-chimice și biologice ale solului. Valoarea optimă de pH a solului pentru creșterea plantelor variază de la o cultură la alta. În general, un sol cu pH-ul 6,0-7,5 este acceptabil pentru majoritatea plantelor, deoarece majoritatea nutrienților sunt disponibili în acest interval de pH. Utilizarea îngrășămintelor minerale, deși benefică și imperativă pentru a obține culturi bune calitativ și cantitativ, modifică pH-ul solului. Această lucrare propune un studiu de laborator privind modificările pH-ului cauzate de utilizarea îngrășămintelor minerale cum ar fi ureea, azotatul de amoniu, îngrășământul complex NPK, combinații ale acestora, cu sau fără adaos de carbonat de calciu. Cercetările au arătat legătura directă între utilizarea îngrășămintelor și modificarea valorilor pH-ului solului.