

Determination of Mobile Phosphorus Fraction in the Soil Variety Taxonomy Using Ammonium Lactate-Acetate

NICOLETA NEMES¹, OANA ALINA COSTESCU¹, VASILE PODE^{2*}, CORNELIU PODOLEANU¹, CONSTANTIN FLORESCU¹

¹Politehnica University Timișoara, Hydrotechnical Engineering Faculty, 1/A G. Enescu Str., 300022, Timișoara, Romania.

²"Politehnica" University Timișoara, Industrial Chemistry and Environmental Engineering Faculty, 2 Victoriei Place, 300002, Timișoara, Romania.

Currently in the case of agrochemical research of the agrarian soils mobile phosphates are calculated, represented by the monophosphate ($H_2PO_4^-$) and diphosphate (HPO_4^{2-}) ions which are usually retained on the soil particles surface associated with sesquioxides, with other minerals components of clay or with the calcium and magnesium ions. Thereby, the mobile phosphates came in contact with the soil solution and determined its concentration in phosphates ions. During the soil evolution, phosphorus from apatite is altered and transformed through precipitation by other secondary minerals or by undertaking by plants or microorganisms in other organical or inorganical phosphor compounds [2]. In the acid soils secondary phosphorus minerals formed contain Al and Fe phosphates, in the type of variscite and strengite [6]. In the neutral and alkaline soils various types of Ca phosphates are found.

Keywords: monophosphate ions, diphosphate ions, sesquioxides, mobile phosphates, primary minerals, secondary minerals

Even if soils contain less phosphor comparative with the others essentials macronutrients (N, K), this element role is highly important, and the chemical processes where it interferes much more complex. Currently phosphorus is considerate a primary macronutrient, with a major role in growing and plant development.

Phosphorus favours nutrition, growing, blossom and fructification processes, depositing carbohydrates in fruits, sugar beet, tubercules. It reduces the typical water consumption of plants. It is accumulated in young organs and seeds. In the absence of phosphorus the plants remain small, the roots are long and rare, the stems are hardened, and the leaves are dark-green till blue-green and in many cases with red or purple color. Besides, the phosphorus involvement in many important processes, the agricultural literature presents numerous examples of cereals and fodder where optimum phosphorus fertility is maintained in the arable soils.

Experimental part

Materials and methods

The mobile phosphorus fraction from soils is determined in ammonium acetate-lactate solution, according to STAS 7184/82.

Range of application:

- method of extractible P determination in ammonium acetate – lactate solution from pH = 3.75 (the Egner – Riehm – Domingo method), conventionally considered a measure of accessible phosphorus (mobile).

- P accessible to the plants nutrition is found as orthophosphate ions (monovalent $H_2PO_4^-$ or bivalent HPO_4^{2-} , depending of soils pH) in the soil and solid soil phase solution (as adsorbed ions or in chemical combinations, mostly with the Fe^{3+} , Al^{3+} , Ca^{2+} ions).

The methods

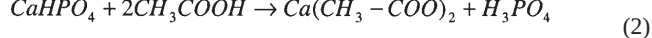
The phosphate anion considered conventionally accessible for the plants is brought to solution by desorption and leaching reaction, dissolution and complexing

reaction, reactions that take place at the ammonium acetate – lactate solution (pH 3.75) with the soil constituents interaction that retain the phosphate anions adsorbing them or contains them as anions in chemical combinations with Fe^{3+} , Al^{3+} , Ca^{2+} ions. The phosphate anion extracted is colorimetric determined as molybdenum blue, through the phosphomolibdenum complex reduction with ascorbic acid or in mixture with reducers.

The phosphates considered easily accessible to the plants are those extracted from soil with a ammonium acetate – lactate solution stippled with pH = 3.7, called AL solution.

The phosphates from soil are found as primary, secondary, tertiary, octocalcium phosphates, adsorbed at the iron or aluminum sesquioxides or clay surface, which is hardly soluble.

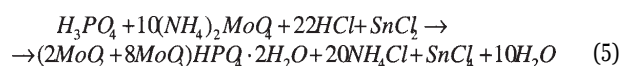
In the neutral and alkaline soils, phosphates are solubilized mostly by the acetic acid which is a component of the AL solution:



In the low acid and acid soils, where a large part of phosphates are retained on the sesquioxides surface, strongly interfere the lactic acid, that has an weak aluminum, iron and calcium complexing action (Al^{3+} , Fe^{3+} , Ca^{2+}):



The phosphoric acid released, treated with ammonium molybdenum in acid environment forms ammonium phosphomolibdate in the presence of a strong reducer ($SnCl_2$) resulting a blue color compound:



* email: vasilepode@yahoo.com

The blue color intensity depends on the solution concentration in H_3PO_4 . Knowing the exact amount of easily accessible forms of phosphates, we can appreciate the soil capacity to supply the plants with phosphorus and phosphorus fertilizers.

Dosing the phosphate anion as „molybdenum blue”

The phosphate anion in solution is determined as molybdenum blue, obtained by the reduction of the phosphomolybdenum complex with ascorbic acid (according to Murphy-Riley method, 1962) [7] or with reducers mixture (ascorbic acid and stannous chloride – according to Nikolov method, 1976) [7].

The variant of dosing according to Nikolov (1976) presents the advantage of a reduced consumption of reagents, a faster color stabilization, being lent with automation dosage. The dosing variant Murphy-Riley (1962) has an advantage for large series of determinations; the colored samples are read at the spectrophotometer the next day.

In this case it was used as analysis method the Nikolov variant.

The sample was photocolimated vs. the witness sample, which did not contain the phosphate anion, but contained all the reagents used for coloring.

On the calibration plot was read the P content adequate for the resulted extinction.

The content of extractable phosphorus (with AL), related to the soil dry by air, is expressed in ppm, thereby:

$$P = \frac{c \cdot r}{m} \quad (\text{ppm}) \quad (6)$$

In the followings is presented the real situation of mobile phosphorus charging of various soil types encountered in the hydrographic basin of the Bistra River perimeter, data resulted from the analysis conducted at the Agrochemical and Pedological Studies.

We can observe from the analysis of tables 1, 2, 3 that in the soil from the Bistra Basin the situation of mobile phosphorus supplying is very weak, the smallest amounts of phosphorus are found in the strong acid soils, data that coincide with the field of study literature. Here the phosphates suffer the immobilization process, due to the reactions caused by Al and Fe ions presence [1, 2, 5, and 6].

The mobile phosphorus supplying of the soils from the western region is negatively influenced by a series of degradation processes of soils from the area and also the phenomenon of phosphates retrogradation, respectively the transformation of phosphates from mobile to immobile forms [4].

The decrease of content of mobile phosphates through absorption of phosphorus in plants and stabilizing of phosphates forms at the soil particles surface is compensated mostly by the mobilization bio-chemical processes, energetically charged by the organic substances that remain in soil as vegetal wastes [1].

All the soils have the capacity to retain phosphorus, excepting the sandy one. The acid soil and the soil with a higher adsorption capacity will bond strongly the phosphate ions.

The alkaline soils contain free $CaCO_3$ that exercises a dominant action over the retaining of phosphate ions, the interception being favored by the pH growth. At higher values of the pH the Ca^{2+} ions activity is high, which favors the phosphate ions interception, through the dicalcium phosphate $CaHPO_4$ transformation in tricalcium phosphate $Ca_3(PO_4)_2$.

Table 1

CONTENT OF MOBILE PHOSPHORUS IN LOW ACID SOILS (ppm)

Eutricambosol			
Orizont	Ao	AB	Bv
Profil 1	42,6	48,6	9,9
Profil 2	13,4	15,5	77,5
Profil 3	141,0	107,7	42,0
Profil 4	189,0	231,2	37,2
Profil 5	34,4	27,2	32,2
Aluviosol			
Orizont	Ao	AC	C
Profil 1	51,9	17,1	23,7
Profil 2	173,0	41,8	20,0
Profil 3	69,7	26,4	13,9
Profil 4	61,8	58,4	30,5
Profil 5	44,8	15,8	27,1

Table 2

CONTENT OF MOBILE PHOSPHORUS IN MODERATE ACID SOILS (ppm)

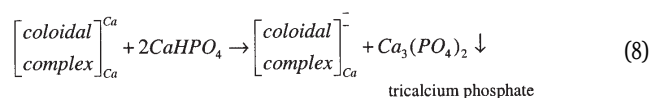
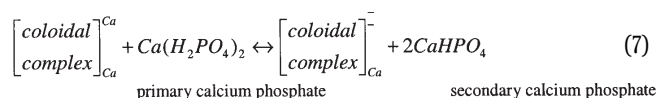
Luvosol tipic			
Orizont	Ao	El	Bt
Profil 1	4,7	6,7	4,7
Profil 2	6,0	5,4	3,5
Profil 3	8,0	4,1	6,7
Profil 4	8,0	4,7	3,0
Profil 5	8,4	6,1	6,7
Luvosol albic			
Orizont	Ao	Ea	Bt
Profil 1	5,4	4,1	6,7
Profil 2	4,1	3,5	3,9
Profil 3	5,4	4,1	6,7
Profil 4	12,2	8,0	8,0
Profil 5	4,1	3,5	2,9

Table 3

CONTENT OF MOBILE PHOSPHORUS IN STRONG ACID SOILS (ppm)

Districambosol			
Orizont	Ao	AB	Bv
Profil 1	4,0	7,3	7,3
Profil 2	3,7	3,5	3,5
Profil 3	3,5	2,9	3,5
Profil 4	4,1	2,9	3,5
Profil 5	3,1	2,5	3,1

The double decomposition reactions that led to the low soluble phosphates insolubility, in the alkaline soil are:



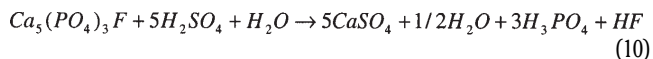
In the neutral and calcareous soils the inorganic phosphorus from soil solution precipitates as *calcium phosphates* after the reaction (4).



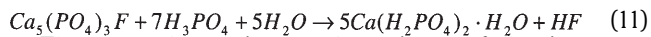
On these types of soils, various phosphorus compounds tend to transform themselves in more stable compounds, like fluorapatite and hidroxilapatite.

Afterwards the primary, secondary and tertiary calcium phosphates transform themselves into more stable forms [2].

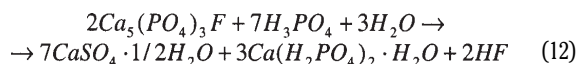
The transformation reaction of the tertiary calcium phosphates in primary calcium phosphates takes place in two phases, according to the following reactions:



The phosphoric acid that forms reaction with the tertiary calcium phosphates that did not enter in the first reaction:



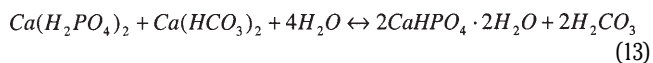
The general equation can be written as following:



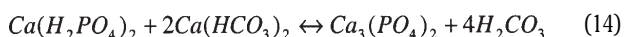
The primary calcium phosphate forms gradually. At first the reaction is rapid, then once $Ca(H_2PO_4)_2$ is formed, the reaction speed decreases, until the solution is oversaturated and it precipitates. The complete tertiary calcium phosphate decomposition or fluorapatite takes a long period of time.

In the alkaline soils the dominant cation is the calcium (positive ion), that will react with the phosphate. A general reaction sequences in the alkaline soil is the formation of dehydrated calcium phosphate, octocalcium phosphate and hidroxilapatite. The formation of each product leads to the solubility decrease and phosphates accessibility.

The easy soluble phosphates fertilizers $Ca(H_2PO_4)_2$, in neutral soils, saturated with bases and especially with calcium, are transformed into secondary calcium phosphates $CaHPO_4$ and tertiary calcium phosphates according to the following reactions:



or



In the acid soils (especially in the case of $pH \leq 5.5$) dominant ion is the aluminum one and this will react with the phosphate. In this case the first product formed will be the aluminum and iron amorphous phosphate and also some calcium phosphates [2]. The aluminum and iron amorphous phosphates are gradually transformed in compounds with similar crystalline structure as the variscite (an aluminum phosphate) and strengite (an iron phosphate) [1]. Each of this reactions will lead to highly instable phosphorus compounds, that generally are inaccessible for plants [1, 3, 4, 6]. The reactions that decrease the phosphorus availability are going in the same way as the soil pH, but can be very pronounced in alkaline soils ($pH > 7.3$) and in acid soils ($pH < 5.5$). Keeping the soil pH between 6 and 7 will determine the highest efficiency in phosphate usage.

In acid soils inorganic phosphorus from soil solution precipitates as aluminum an iron phosphate [3], according to the reaction:



On the soil with acid reaction, the iron, aluminum and manganese are highly mobile and the phosphoric ions precipitations take place as sesquioxides phosphates [2], the chemical retain is made according to the following reactions:



or



This way is retained most of the phosphorus added as fertilizer in the acid reaction soil. If the soil reaction is corrected through liming and the pH becomes almost neutral, the phosphoric ions strongly retained by $Fe(OH)_3$ and $Al(OH)_3$ are easily released.

Conclusions

For most of soil types, the phosphates fraction from the soil solution precipitates in the form of various calcium, aluminum, iron phosphates, depending on the existent acidity soil conditions.

The synthesis of agrochemical mapping regarding the mobile phosphorus supplying of soils from the western part of Romania shows a large degree of phosphorus provision under optimum value (30-35 ppm P_{AL}).

In the context of normal soil exploitation, without phosphates or inorganically fertilizers, a decrease of mobile phosphates in arable layer takes place. That happens through phosphorus consume for cropping and by an thermodynamic evolution, as a result of complex physical and chemical processes that determine the decrease of free energy from the phosphates.

Note

c = content of P in the colorimetric sample, established from the calibration plot (μg);

r = the ratio between the volume of the solution used in extraction and the extract volume taken with the dropping glass for the phosphorus dosage;

m = the sample soil mass taken in works (g).

Acknowledgments: The present work has been supported from the National University Research Council Grant (CNCSIS) PNII, ID 34/77.01.2007: MODELS DEVELOPMENT FOR THE EVALUATION OF MATERIALS BEHAVIOUR TO CAVITATION

Bibliography

1. DARKE, A.K., WALBRIDGE M.R, Al and Fe biogeochemistry in a floodplain forest: implications for P retention. *Biogeochemistry* 2000, (51:1-32).
2. HILLEL, D., *Encyclopedia of soils in the Environment*, Elsevier Academic Press, 2000.
3. ROGOBETE, Gh., NEMEȘ N., CONSTANTINESCU, L., NEMEȘ, I., Phosphorus Retention and Mobility in Some Acid Soils in South-Western Romania – Scientific Bulletin of "Politehnica" University from Timișoara, *Transaction on Hydrotechnics*, 2005, (p.33-37).
4. ROGOBETE, Gh., NEMEȘ, N., Mobile Phosphorus Contents In Some Acidic Soils In Bistra Hydrographic Area - Scientific Bulletin of "Politehnica" University from Timișoara, *Transaction on Hydrotechnics*, 2005, p. 162
5. RUSU, M., MĂRGHITAȘ, M., OROIAN, I., MIHĂILESCU, T., DUMITRAȘ, A., *Agrochemical handbook*, Ed. Ceres, București, 2005
6. SMECK, N.E., *Phosphorus dynamics in soils and landscapes, Stream Corridor Restoration: Principles, Processes, and Practices*. 1998 (revised 08/2001). The Federal Interagency Stream Restoration Group (FISRWG), 1985, *Geoderma*. 36, p 185
7. STOICA, E., RĂUȚĂ, C., FLOREA, N., *Methods of chemical analysis of soil*, ICPA București, 1986

Manuscript received: 8.12.2008