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RESEARCH THE AMELIORATIVE EFFECT OF PRECIPITATE ON pH VALUES ACCORDING TO THE PROFILE OF GENETICALLY ACID SOILS

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Abstract

In the present study, the effect of the precipitate as a chemical ameliorant on the changes of the values of the pH indicator along the depth of the soil profile was studied. Its interaction with the soil was also associated with the release of Ca^{2+}, which was due to its prophylactic chemical-ameliorative effect in acidic soils. The movement of the precipitate along the depth of the soil profile and in general the migration of this compound into the soil volume was very limited, both with respect to the phosphate and the calcium component. Better penetration into the deep soil horizons was observed at constant humidity close to utmost field moisture content and at soils with a high rate of natural water filtration.

***Key words**: acid soils, pH, precipitate, soil profile.*

INTRODUCTION

The principle of ameliorative effect of the precipitate applied in acid soils is based on its neutralizing activity. It manifests itself on two levels - direct acid neutralizing action of the accompanying main compound $CaCO_3$ and the neutralizing action of calcium cations contained in the molecule, which after the absorption of phosphorus remain in the soil and are included in the sorbent.

In medium and high absorbing soils the calcium ions released in the process of phosphate absorption charge, neutralize and from the colloid-disperse point of view stabilize the colloidal complex in the soil, causing permanent coagulation of its mineral and organic components.

In conditions of strong calcium deficiency, as a nutrient chemical element, the application of a precipitate solves the problem of mineral nutrition of the plants with calcium even when applied in limited doses. Based on this mechanism, some manufacturers recommend the application of the precipitate off-root (Trendafilov, 2011).

In the present study the effect of precipitate as a chemical ameliorant on the changes of the values of the pH indicator along the depth of the soil profile was studied.

MATERIALS AND METHODS

The experiment was carried out for two years on Chromic luvisols with differentiated profile. A precipitate was used as the main chemical ameliorant. Calcium hydrogen phosphate dihydrate ($CaHPO_4$ x $2H_2O$) is used as a mineral citrate-soluble phosphorus fertilizer in various soils and crops. Contains 25-40% P_2O_5, depending on the quality of the raw material in its production. The advantage of its use is related to its longer-lasting fertilizing effect compared to superphosphates. Its interaction with the soil is also associated with the release of Ca^{2+}, which is due to its prophylactic chemical-ameliorative effect in acidic soils. The rates in which it is applied to cover the needs of annual agricultural plants for phosphorus fertilization have a weak chemical-ameliorative effect and are usually not sufficient to neutralize the harmful acidity in the soil. It can be applied as a phosphorus fertilizer for storage fertilization before deep ploughing the terrains intended for planting perennial crops.

The experiment was based on the method of long plots (Shanin, 1965), and the distribution of variants included control variant and three increasing rates of treatment with precipitate - 100, 250 and 500 kg/ha. Each of the variants is performed in three repetitions.

After application, the ameliorant is incorporated at a depth of 18-20 cm in the soil, and before that with surface treatment it is homogenized with a workable layer with a depth of 10-12 cm. This application model requires no more than routine tillage in perennials and is not associated with additional costs, as with the application of chemical ameliorants in high doses. Soil samples were taken twice, with the first sampling 14 months after the application of the ameliorant, and the next one 12 months later. Soil samples were taken from three layers with a depth of 0-25; 25-50 and 50-75 cm, using a soil probe, as the volume of each soil sample is composed of 3 single receivables with the probe within the area of each replication. Soil samples were analyzed to determine pH, potentiometric in water and in salt extract-1 n KCl (Arinushkina, 1970).

RESULTS AND DISCUSSIONS

Because the pH affects PO_4-P sorption/ desorption to soil components (Haynes, 1982), prediction of the pH effect is important for correct estimates of PO_4-P solubility in a soil subject to pH changes. The processes governing the sorption and desorption of PO_4-P in soils are several. Adsorption to the surfaces of iron(III) and aluminium (hydr)oxides is known to be important. In addition, PO_4-P may be adsorbed also to hydroxy-Al polymers in clay minerals (Karathanasis and Shumaker, 2009) and to carbonate minerals (Yagi and Fukushi, 2011). Because PO_4-P adsorption increases with decreasing pH, these adsorption processes would often be expected to be more influential at low pH (Goldberg and Sposito, 1984), resulting in a "positive" pH dependence (i.e. increased PO_4-P solubility at higher pH), provided that adsorption is fully reversible within the time scale of interest.

Precipitation of PO_4-P with Ca is expected at higher pH. A number of Ca-P minerals may form, such as amorphous calcium phosphate (ACP), octacalcium phosphate (OCP) and apatite (hydroxyapatite, HAp, or fluorapatite, FAp). Precipitation/dissolution of these minerals will cause a "negative" pH dependence (increased PO_4-P solubility at lower pH) (Hesterberg, 2010).

Prior to the application of the ameliorant, pre-sampling was performed in three depths of 0-25, 25-50 and 50-75 cm and the pH values in aqueous and salt extract were determinate. The pH is usually determined potentiometric on pre-dried soil samples. The measurement of pH in a soil suspension is preferred to this in an aqueous extract due to its greater proximity to the conditions in the natural soil (Amelyanchik and Vorobieva, 1991; Vozbutskaya, 1985).

Figure 1 shows that the pH values in both aqueous and salt extract were acidic, as the decrease in depth was insignificant. The soil: water ratio affects pH values not only by affecting the suspension effect, but also by altering the acid-base balance. The suspension effect decreases with increasing amount of the aqueous phase and is the reason for the lower pH values in the soil suspension than in the aqueous extract (Faitondjiev, 2008).

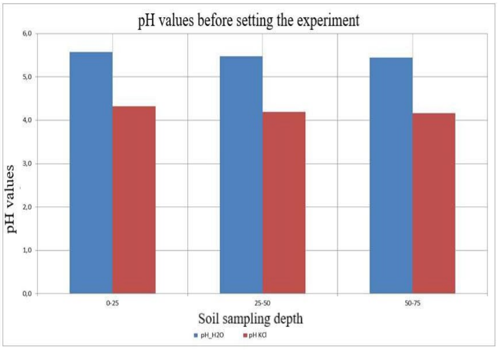

Figure 1. pH values before setting the experiment

After the application of calcium precipitate as an ameliorant, both in the low and in the high doses led to a relatively small change in the pH indicator in both variants of its measurement - in water and in potassium chloride. The values of the change in pH as a result of the application of precipitate did not prove a statistically significant change in the indicator, although there was a tendency that when apply the precipitate as calcium ameliorant the lowest pH values found in the strongly acidic soil area had a tendency for a change towards a medium to slightly acidic reaction. The influence of the precipitates in the top soil horizons was relatively strongest during the first soil sampling.

No influence was established in the deep horizons and this was because of the difficult and slow infiltration of the ameliorant into the depth. The limited doses of the applied ameliorant explained the established decrease in the effect of the calcium precipitate in the second year after its introduction.

The change in pH measured in water (Figure 2) compared to that in the potassium chloride (Figure 3) extract showed that in the salt extract the data had less scattering and were obviously less affected by the impact of the ameliorant.

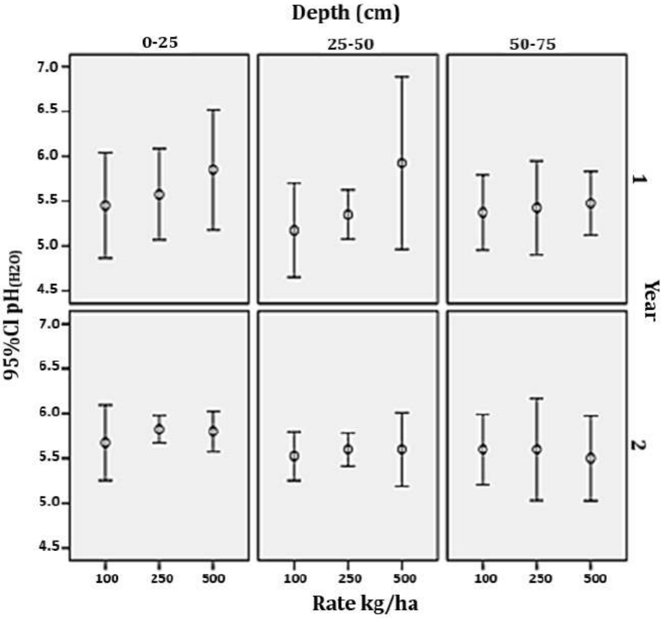

Figure 2. Change in pH$_{(H_2O)}$ at different depths in the soil depending on the amount of the applied precipitate and the measurement time

The pH indicator (KCl) is generally considered to be a more conservative indicator insofar as it characterizes the equilibrium of the constant sorption positions in the soil absorption complex and is less influenced by random factors (Valcheva, 2020).

This is explained by the fact that in the salt extract the balance of the acidic and alkaline component is determined by relatively higher ionic concentrations, and some of the ions that determine it originate from positions in the exchange complex on the easily mobile ions in the sorbent.

The short ameliorative effect is explained by the stability of the acid-alkaline balance in the acidic area and the fact that it was a genetic characteristic based on the high capacity of the buffer system in the soil, representative of the forest soil complex.

Both precipitation and adsorption reactions are involved in the retention mechanism of phosphates. When the orthophosphate concentration is low, the dominant process is the adsorption of phosphate ions onto the surfaces of more crystalline clay compounds, sesquioxide’s, or carbonates (Plante, 2007; Gerard, 2016; Whalen and Sampedro, 2010).

On the contrary, when the orthophosphate concentration is high, soluble P precipitates with metal cations to form Fe and Al phosphates in acidic soils, and Ca and Mg phosphates in alkaline soils (Smith, 2003; Plante, 2007; Whalen and Sampedro, 2010). It is believed that the adsorption process is essential in managing the availability of Ca and P over a shorter time frame (Smith, 2003). When soluble Ca is applied to soils in the forms of fertilisers or amendments, a rapid increment of soil solution concentration is noted. Afterwards, these portions undergo precipitation or adsorption processes to decrease their solubility (Power and Prasad, 1997). These chemical reactions are pH dependent. In acidic soils, Al and Fe ions usually form precipitates with approximately all the dissolved H_2PO_4 - ions. These precipitated hydroxyl phosphates are insoluble, thus, their P content becomes almost unavailable to plants. The pH change data presented as a function of the ameliorative intervention with the precipitate are shown in Figures 4 and 5.

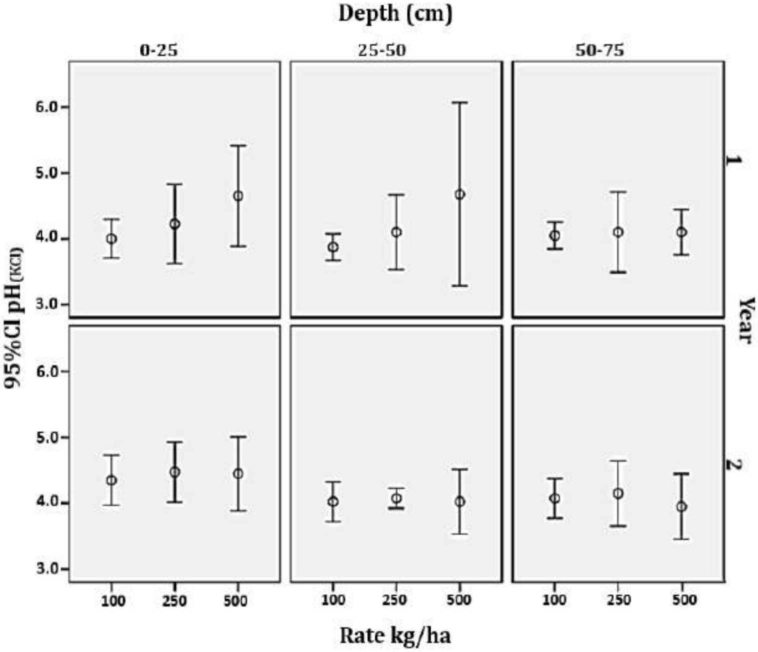

Figure 3. Change in $pH_{(KCl)}$ at different depths in the soil depending on the amount of the applied precipitate and the measurement time

The high pH values found in the first year of measurement were due to the partially undissolved and incompletely interacted with the soil absorption complex Ca^{2+} from the precipitate. The fact that this increase in pH was found along the entire depth of the ameliorated layer showed that the applied at the ameliorative experiment technology of ameliorants application was successful and achieved its penetration into depth. Over time, the applied with the ameliorative materials Ca^{2+} has connected in exchange form, determining a relatively stable acid equilibrium, characterized by pH values in the weakly acidic area.

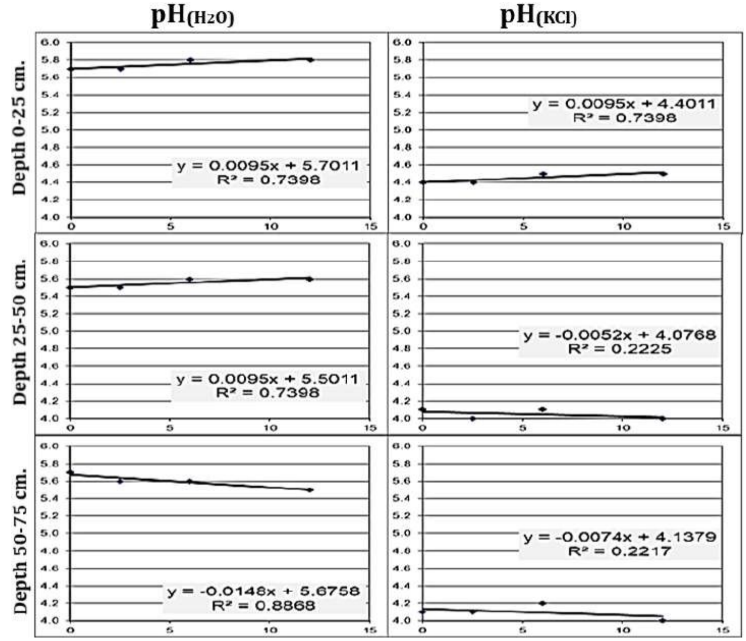

Figure 4. Change in pH$_{(KCl)}$ and pH$_{(H_2O)}$, depending on the amount of the applied precipitate at different depths in the soil in the first year after the application of the ameliorant

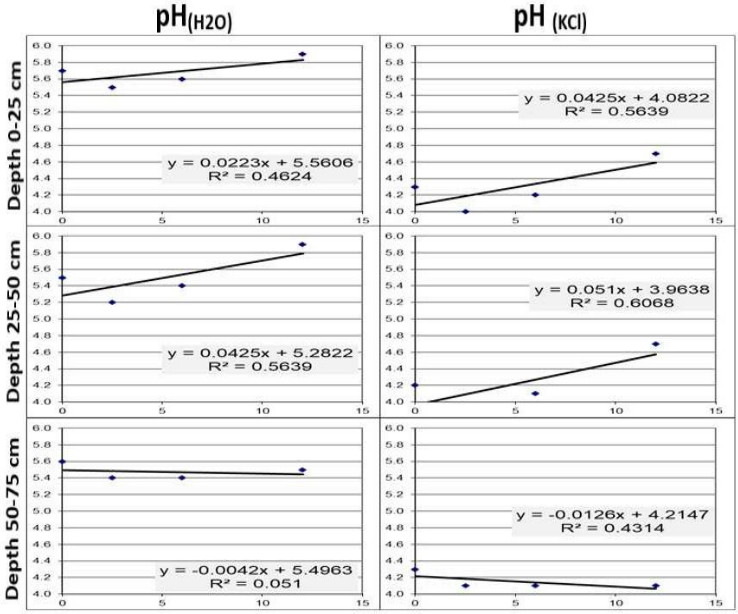

Figure 5. Change in pH$_{(KCl)}$ and pH$_{(H_2O)}$, depending on the amount of the applied precipitate at different depths in the soil in the second year after the application of the ameliorant

CONCLUSIONS

The movement of the precipitate along the depth of the soil profile and in general the migration of this compound into the soil volume was very limited, both with respect to the phosphate and to the calcium component. Better penetration into the deep soil horizons was observed at constant humidity close to utmost field moisture content and at soils with a high rate of natural water filtration.

Its agrochemical effect was comparable with other weakly soluble fertilizers in terms of the mechanism of interaction with soil components and as assimilation. For this reason, the results of its experimental application were extrapolated with those that would be obtained by application of similar chemically phosphorus-containing fertilizers (ameliorants) - phosphorus flours or granules, Thomas flours and others, as long as the ratio of phosphorus to calcium is similar to that of the precipitate.

REFERENCES

Amelyanchik, O. A., Vorobyeva, L. A. (1991). Indicators and methods for assessing soil acidity and soil demand for lime. *Agrochemistry, 2*. 123–135.

Arinushkina, E. V. (1970). Guidance for Chemical Analysis of Soils. *Moscow State University Publishing House.*

Faitondjiev, L. (2008). Problems of acidity and liming of soils. *Soil Science, Agrochemistry and Ecology*, Sofia, *2*. 3–16.

Gerard, F. (2016). Clay minerals, iron/aluminum oxides, and their contribution to phosphate sorption in soils- A myth revisited. *Geoderma*, *262*. 213–226.

Goldberg, S., Sposito, G. (1984). A chemical model of phosphate adsorption by soils. 1. Reference oxide minerals. *Soil Science Society of America Journal, 48*. 772–778.

Haynes, R. J. (1982). Effects of liming on phosphate availability in soils. *Plant Soil*, *68*. 289–308.

Hesterberg, D. (2010). Macroscale chemical properties and X-ray absorption spectroscopy of soil phosphorus. In: Singh, B., Gräfe, M. (Eds.), Synchrotron-based techniques in soils and sediments. *Developments in Soil Science*, *34*. 313–356.

Karathanasis, A. D., Shumaker, P. J. (2009). Organic and inorganic phosphate interactions with soil hydroxyinterlayered minerals. *Journal of Soils and Sediments*, *9*. 501.

Plante, A. F. (2007). Soil biogeochemical cycling of inorganic nutrients and metals. In Soil Microbiology, Ecology and Biochemistry; Academic Press: *Cambridge,* MA, USA, 389–432.

Power, J. F., Prasad, R. (1997). Soil Fertility Management for Sustainable Agriculture. CRC Press: *Boca Raton*, FL, USA, 1997.

Smith, V. H. (2003). Eutrophication of freshwater and coastal marine ecosystems a global problem. *Environ. Sci. Pollut. Res*., *10*. 126–139.

Trendafilov, K. (2011). Influence of storage fertilization with precipitate ($CaHPO_4$ x $2H_2O$) on the acid-alkaline balance in the soil and the chemical composition of wine grape varieties. *Scientific reports from the International Conference 100 years of soil science in Bulgaria*, second part, 16-20 May, Sofia, 669–674.

Vozbudskaya, A. E. (1964). Soil Chemistry. Moscow.

Valcheva, V. (2020). Influence of the liming on the soil and morphological indicators of lavender grown in organic agriculture. *Knowledge International Journal Scientific Papers*, *41*(4), 759–770, ISSN: 2545-4439.

Whalen, J. K., Sampedro, L. (2010). Soil Ecology and Management. CABI: *Wallingford*, Oxford, UK, 2010.

Yagi, S., Fukushi, K. (2011). Phosphate sorption on monohydrocalcite. *Journal of Mineralogical and Petrological Sciences*, *106*. 109–113.