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SOIL MANAGEMENT IN AGROECOSYSTEMS - IMPACT ON THE CATION-ANION COMPOSITION IN THE AERATION ZONE OF SOILS

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ABSTRACT

The research aimed to analyze the cation-anion composition of the soil solution in dark-grey podzolized soil under the influence of long-term anthropogenic factors. Over the extended application of both mineral and organic fertilizers, changes in the cation-anion composition of the soil were observed, depending on the dosage of mineral fertilizers and their distribution within the soil profile. When the amount of mineral fertilizers was increased from 265 kg NPK per hectare to 397 kg per hectare, a noticeable decrease in soil solution pH was observed, with pH levels dropping to 6.1 and 6.0, as compared to the control variant without any fertilizer application, which exhibited a pH of 6.3. The application of mineral fertilizers and manure additionally enriched the soil with ions of organic and inorganic acids, what became the reason for the redistribution between mobile and immobile forms of calcium and magnesium in the direction of increase of their mobility beyond the soil profile. The greatest accumulation of sulphate was observed at a depth of 160–280 cm due to the migration of their water-soluble forms. The main quantity of chlorine was moved and accumulated in the soil layer of 120–280 cm, and the increase of mineral fertilizers increased the content of chlorine in the aeration zone.

Keywords: cation-anion composition, agroecosystem, fertilization, dark-grey soil, exchange acidity, migration.

INTRODUCTION

Soil resources are the basis of agricultural production. Modern, high-intensity technologies for growing agricultural crops are effective on soils with high fertility rates. Well-cultured soils are specific natural-anthropogenic formations. They are characterized by high buffers and resistance to deterioration of the acquired parameters, and on the other hand, their agrochemical properties due to natural conditions of soil formation are constantly tending towards the initial genetic condition.

With the increase of anthropogenic impact on the soil, the relationships in the soil-plant system are becoming more complicated, and the issue of soil interaction in the ecological system is topical (Symochko et al., 2021; Symochko et al., 2023; Litvinova et al., 2023). It should be noted that the process of degradation of acid-alkaline soil properties determined by the chemical composition of the maternal rock and by the level of application of fertilizers, especially nitrogen, by the removal of calcium with the harvest and its leaching from the soil profile (Bartkowiak et al., 2016; Smith et al., 2016). Optimizing mineral nutrition is possible under the condition of ensuring the appropriate level of physical and chemical properties of the soil, which is characterized by the reaction of the environment, the amount and composition of exchangeable cations, the capacity of the soil absorption complex, its saturation with bases and determines the mobility of cations and anions in the soil solution (Degodyuk et al., 2015; Tkachenko et al., 2018; Degodyuk et al., 2020). Chemical melioration is an important factor in improving soil fertility and fertilizer efficiency. Its carrying out contributes to the improvement of physical and chemical properties of soils, provision of plants with calcium and magnesium, intensification of microbiological processes, and reduction of accumulation of radionuclides in plant production (Korsun and Klymenko, 2018; Litvinova et al., 2018). But not only the quantitative composition of the selected bases solves the fertility of soils. An important indicator is the ratio in the SAC (soil-absorption complex) between calcium and magnesium. M. M. Horodnii, etc. (Horodnii et al., 2008) believe that this ratio should be 1:4. With increased particles of magnesium concerning calcium, the fertility of soils is reduced due to increased solution of humus substances, and since magnesium humates are toxic, they paralyze the development of plant roots. Studies of scientists have found that the optimal ratio between calcium and magnesium for different field cultures varies sharply and varies between 40 and 80 parts of magnesium per 100 parts of calcium (Tkachenko et al., 2018; Dmytrenko and Pavlichenko, 2020) also, calcium actively participates in many soil processes related to humus formation (Degodyuk et al., 2019; Boyko et al., 2019). The most important parameters of soil fertility, which reflect well the specifics of the soil-forming process and peculiarities of its mineral parts composition, as well as the content and composition of humus substances, are the sum and composition of the exchange bases, the content of hydrogen and aluminium ions, the magnitude of hydrolytic acidity and pH. Limiting and organic resources create a favourable reaction in the soil and strengthen biological activity in it (Demyanyuk et al., 2019; Litvinova et al., 2019; Demyanyuk et al., 2020). This affects the nature and rate of decomposition of organic fertilizers in the soil, and the speed of use by plants of nutrients contained in them (Litvinova et al., 2021). Carbon dioxide released during the decomposition of organic fertilizers promotes the transition of carbonates into bicarbonates, and humus substances formed from organic fertilizers together with lime have a beneficial effect on improving the physical properties of the soil (Demyanyuk et al., 2019). With application of agrochemicals, soil properties, mobility and accessibility of macro- and microelements are largely changed (Bondar et al., 2019; Litvinova et al., 2020; Makarenko et al., 2021). Everything that is applied to the soil reacts with other components, and for effective production, a balanced physicochemical calculation and forecast of the processes taking place in it are necessary. Systematic use of organic and mineral fertilizers, to a certain extent, provides optimal physical and chemical properties of soil, namely, the cation-anion composition of the soil solution (Kozlov et al., 2003). However, it is possible to note the contradiction of views on the effectiveness of complex application of chemicals. This work aimed to study the effect of the systematic application of mineral and organic fertilizers in crop rotation on the change in the cation-anion composition of the soil solution of dark-grey podzolic soils.

MATERIAL AND METHODS

Field research was carried out in a long-term stationary experiment, established in 1987 on a dark-grey podzolic soil. The soil was characterized by the following agrochemical indicators: pHкcl-5,2, hydrolytic acidity – 3,9, and the number of absorbed bases – 12,5 mg-eq. per 100 g of soil, the content of total humus – 2.0%, mobile phosphorus (according to Chirikov) – 160 mg P_2O_5 per kg of soil, mobile potassium (according to Maslova) –140 mg K_2O per kg of soil. Crop rotation in the experiment was 8-pole grain–row: peas, winter wheat, sugar beets, spring barley, corn for silage, winter cereals (wheat, triticale, rye), corn for grain, and oats. The square of the sowing area is 42 $м^2$, and the accounting area is 25 $м^2$. The repetition in the experiment is four times. Cattle manure was used for sugar beets and corn for grain at the rate of 40 t/ha. The test crop is peas of the Intensivny-92 variety. The research was conducted on the 3 most contrasting fertilizer options: 1 – Without fertilizers (control); 2 – 10 tons of manure per 1 ha of arable land + $N_{86}P_{80}K_{99}$; 3 – 10 tons of manure per 1 ha of arable land + $N_{129}P_{120}K_{148}$. By the purpose and tasks, the following studies in soil samples are provided: pHкcl – potentiometrically (DSTU ISO 10390:2001);

determination of exchangeable cations of calcium and magnesium by the trilonmetric method; method of determination of sulphate content (GOST 4389-72); determination of chlorine by Mohr's method.

Statistical analysis.
The least significant difference at $P < 0.05$. Statistical processing was performed by Microsoft Excel in combination with XLSTAT.

RESULTS AND DISCUSSION

One of the main problems of the arable land in Ukraine is the reduction of fertility caused by the acid degradation or decalcification of soils. As a result of such processes, there is a significant deterioration of the physical and chemical properties of soil, a reduction of available forms of biological and alkaline-earth soil elements for plants. In the recent years acid precipitation cause deep negative changes in various components of ecosystems, including in soils. In conditions of light granulometric composition of the soil, the inflow to the arable layer of organic and mineral compounds in the form of fertilizers, meliorants, pesticides can cause redistribution between movable and bound forms of cations and anions in all soil profiles. The proximity of the first tier of soil waters (3,60–4,50 m) makes it necessary to study not only the standard soil profile (116–120 cm) but also the entire zone of aeration with a capacity of up to 3,60 m. For these purposes three options of fertilizer were chosen: without fertilizer (var. 1), with moderate saturation with mineral fertilizers $N_{86}P_{80}K_{99}$ and 10 tons of manure per 1 ha of arable land (var. 2), the option with maximum saturation with mineral fertilizers $N_{129}P_{120}K_{148}$ and 10 tons of manure per 1 ha of arable land (var. 3).
The analysis of the amount of the exchange acidity of the soil environment allows concluding about the ratio of exchange cations and anions. The results of the research showed that the exchange acidity of soil depended on the level of agrochemical loading, and the depth of the layer of soil in the aeration zone (fig. 1).

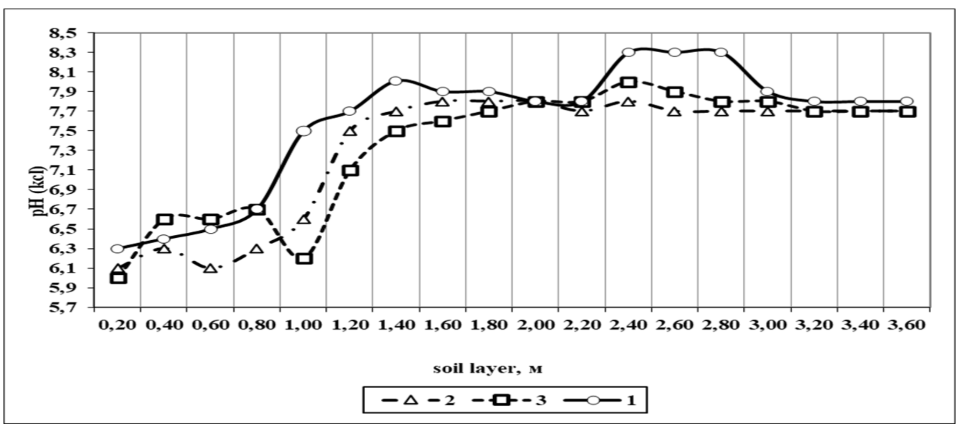

Figure 1. Change of the exchange acidity (pHкcl) in the soil profile of dark-grey podzolic soil, depending on fertilizer options
Fertilizer option: 1 – Without fertilizers (control); 2 - 10 tons of manure per 1 ha of arable land + $N_{86}P_{80}K_{99}$; 3 – 10 tons of manure per 1 ha of arable land + $N_{129}P_{120}K_{148}$

On all the investigated variants, the exchange acidity was the highest in the soil layer (0–20 cm), and with the increase of mineral fertilizers norm from 265 kg NPK per 1 ha of the crop rotation area to 397 kg/ha it grew from pH 6,1 to pH 6,0. With depth acidity sharply decreases, although the acidifying effect of mineral fertilizers is left perceptible in the whole investigated layer of soil.
Optimization of the SAC state due to the simultaneous increase of concentration of calcium and magnesium is possible due to the use of organic fertilizers, calcareous materials, and mineral fertilizers, which include these cations (Melnyk et al., 2012). Four limiting have been conducted since the investigation was established. The calcareous materials were applied in the same quantity in all areas of the investigation, therefore at the general improvement of physical and chemical properties and the living regime of the soil, there is an opportunity to trace

the influence of different fertilizer systems on formation of the SAC in general, and on the provision of the soil by movable forms of calcium and magnesium. Studies have shown that the application of cattle manure in intensive fertilizer systems ($N_{129}P_{120}K_{148}$) contributed to a greater accumulation of calcium in the layer of 0-40 cm with variants, where, besides organic fertilizers, introduced moderate norms of mineral fertilizers ($N_{86}P_{80}K_{99}$). This is due both to the return of calcium bound by organic matter to the soil, and to a much smaller removal of it by the marketable part of the crop. In contrast to calcium, no special changes in the content of exchangeable magnesium, depending on the fertilizer, were recorded. Its content in the 0-20 cm layer is 0,69-0,80 mg-eq/100 g of soil. It was established that with the application of mineral fertilizers against the background of 10 t/ha of manure, a decrease in the number of exchangeable forms of calcium and magnesium is observed both in the upper 20 cm soil layer and in the root layer of the soil. Thus, in the 0-20 cm layer of the soil, depending on the rate of mineral fertilizers, the content of mobile calcium decreased compared to the option without fertilizer by 5% when applying 397 kg of NPK per 1 ha and by 18 % when applying 265 kg of NPK per 1 ha. Regarding mobile magnesium, its content decreased by 30 and 38 %, respectively. The peculiarity of the structure of the soil profile of dark grey podzolic soils, in the presence of the parent rock (forest-like loam), causes a tendency to increase the content of cations in the lower horizons (120–360 cm), but excessive loads of agrochemicals influenced the strengthening of leaching processes in the soil aeration zone.

However, the most important aspect is its ratio to calcium. According to scientists, there will be no shortage of magnesium if the equivalent ratio between calcium and magnesium is equal to six (Litvinova et al., 2018; Hilger et al., 2020). According to the results of our research in the areas for the use of fertilizer, the recommended ratio is broken, and its value exceeds 7, which testifies to the deepening deficiency of accessible forms of magnesium in the soil. Long-term use of soil in earthmoving for different agrochemical loading has led not only to the formation of soil funds with different living conditions but also to changes in the soil-absorption complex (SAC). Thus, the application of mineral fertilizers and manure (options 2 and 3) additionally enriched the soil with anions of organic and inorganic acids, which, in turn, caused a redistribution between mobile and immobile forms of calcium and magnesium in the direction of increasing their mobility, which could be the reason for their partial migration beyond the soil profile (Figs. 2 and 3). Losses of calcium and magnesium from the arable layer of the soil are largely caused by the application of physiologically acidic fertilizers, especially increased doses, their acidifying effect is manifested not only in a negative effect on acidity indicators, but also in the strengthening of calcium and magnesium leaching processes, a decrease in the effectiveness of applied fertilizers and a decrease in yield increases (Mazur, et al., 2019).

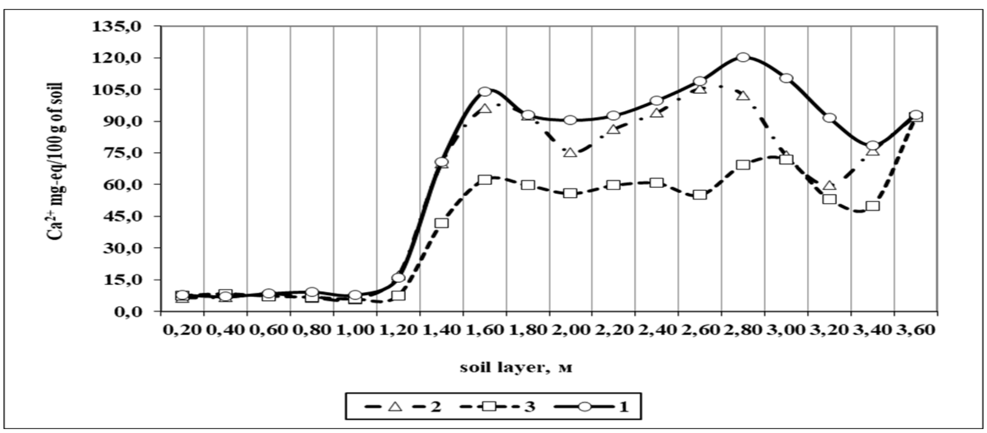

Figure 2. Distribution of Ca^{2+} in the aeration zone of dark-grey soil, depending on the fertilizer options, mg-eq/100 g of soil

Fertilizer option: 1 - Without fertilizers (control); 2 - 10 tons of manure per 1 ha of arable land + $N_{86}P_{80}K_{99}$; 3 - 10 tons of manure per 1 ha of arable land + $N_{129}P_{120}K_{148}$

Therefore, the size of the losses of absorbed bases caused by leaching depends on the nature of the territory's moisture, the degree of acidity of the soil solution, the crop fertilization system, and the biological characteristics of the crops. Thus, the infiltration of mobile soil compounds is influenced by numerous factors, which in most cases are interconnected and act simultaneously.

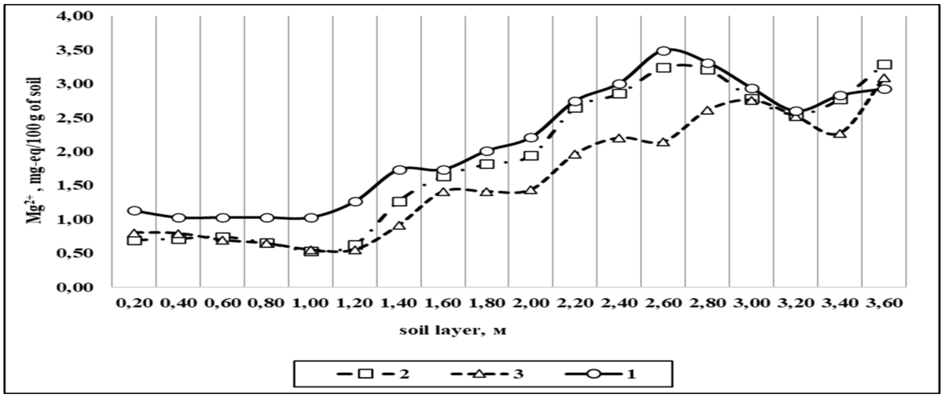

Figure 3. Distribution of Mg2^{+} in the aeration zone of dark-grey soil, depending on the fertilizer options, mg-eq/100 g of soil.

Fertilizer option: 1 - Without fertilizers (control); 2 - 10 tons of manure per 1 ha of arable land + $N_{86}P_{80}K_{99}$; 3 - 10 tons of manure per 1 ha of arable land + $N_{129}P_{120}K_{148}$

It is possible to speculate about the leaching of calcium and magnesium into the groundwater, since along with the depletion of calcium and magnesium in the fertilized variants, a sharp increase in the number of water-soluble sulphates was observed (Fig. 4), which was probably previously bound in a difficult solution in a neutral salt environment calcium. Thus, mineral substances in arable lands migrate mainly in the form of sulphates, chlorides and bicarbonates of alkaline earth and partially alkaline bases. The removal of these substances from the soil profile, along with the intensity of its washing, is influenced by the level of agricultural technology – the amount, type, time and method of applying fertilizers and lime, the nature of soil treatment and cultivated field crops (Tkachenko M.A., Boris N.E., 2020). It should be noted that the ions of anions are not brought to the soil colloid, which explains their high mobility in the soil, they are not adsorbed by its colloidal particles and are easily washed out. The largest accumulation of sulphates was observed at a depth of 160–280 cm due to the migration of their water-soluble forms from exceeding the maximum allowable concentration (160 mg/kg) (Petruk V.G., et al., 2019). In the case without organic and mineral fertilizers (var. 1), on the contrary, there was a decrease in the content of sulphates due to their binding into poorly soluble calcium compounds.

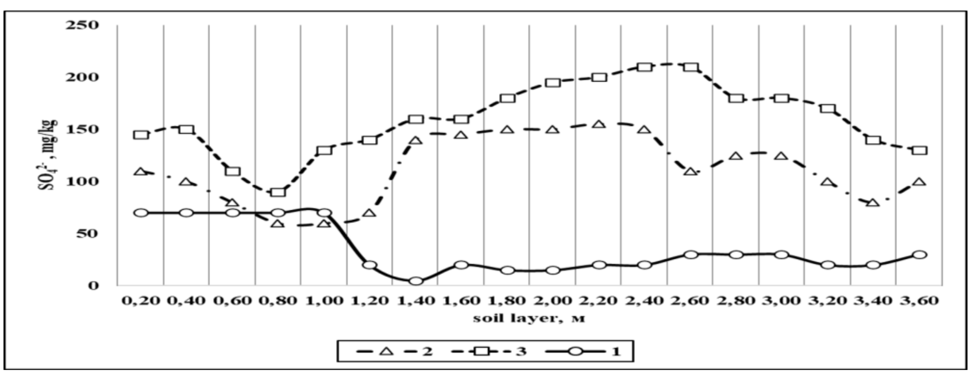

Figure 4. Change in the content of SO_4^{2-} in the aeration zone of dark-grey soil depending on the fertilizer options, mg/kg.

Fertilizer option: 1 - Without fertilizers (control); 2 - 10 tons of manure per 1 ha of arable land + $N_{86}P_{80}K_{99}$*; 3 - 10 tons of manure per 1 ha of arable land +* $N_{129}P_{120}K_{148}$

An important reason for the decrease in the content of water-soluble sulphates in the aeration zone of the variant without fertilizers was the removal of sulphur from the soil by agricultural plants, since sulphur is a necessary biogenic element that is part of proteins, enzymes and vitamins (Grzyb et all., 2021). A similar pattern was observed for chlorine (Fig. 5), which enters the soil with fertilizers and meliorants. It is known that chlorine is characterized by a high migratory ability to move along the soil profile and does not form stable complex bonds with its mineral

and organic components, and is also weakly sorbed on the surface of soil particles. Therefore, if Cl- ions can penetrate the lower layers of the soil, then SO_4- ions of fertilizers will also migrate to this depth.
Applying high doses of potash fertilizers can lead to an increased concentration of chloride ions, disrupt the ratio between cations $Ca^{2+:}$ K^+, Mg^{2+}, K^+, displace calcium and magnesium from the soil complex, and also increase their migration along the soil profile.

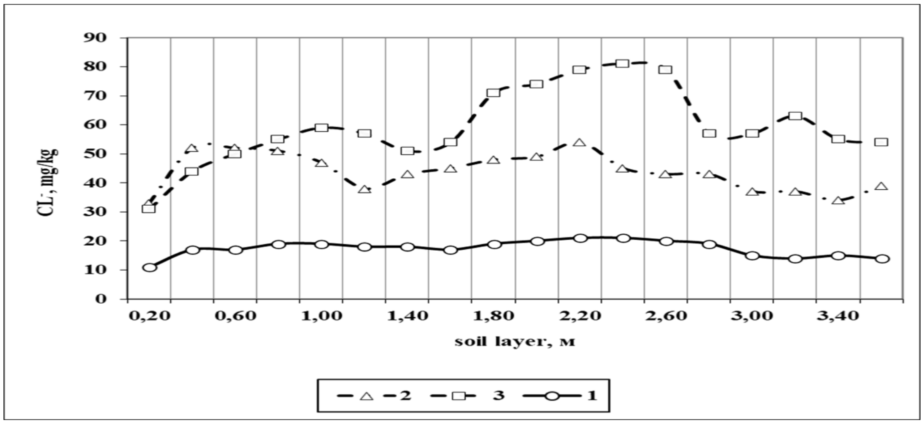

Figure 5. Change in the content of CL^- in the aeration zone of dark-grey soil, depending on the fertilizer options, mg/kg

Fertilizer option: 1 – Without fertilizers (control); 2 – 10 tons of manure per 1 ha of arable land + $N_{86}P_{80}K_{99}$*; 3 – 10 tons of manure per 1 ha of arable land +* $N_{129}P_{120}K_{148}$

The share of chlorine in the arable layer (0–20 cm) was 4–13 % of its total increase in the aeration zone. The main amount of chlorine moved and accumulated in the soil layer of 120–280 cm, and increasing the dose of mineral fertilizers increased the chlorine content in the aeration zone (var. 2 and 3). Given the mobility of chlorine and its tendency to wash out in areas where the soil is poor in chlorine (sandy and light loamy), the effect under appropriate conditions from the application of chlorine-containing fertilizers will be higher.

CONCLUSIONS

The long-term studies in the agroecosystems have shown that with the application of organic and mineral fertilizers, changes in the cation-anion composition of the soil solution occur not only in the arable layer of the soil but also in the entire aeration zone of the dark-grey podzolic soils up to the level of the first layer of groundwater. Uncontrolled application of fertilizers with an increase in their load per unit area up to 397 kg of NPK (per 1 hectare of crop rotation area) in agriculture can disrupt the natural saline composition of groundwater, causing its chemical pollution, which affect the agroecosystem. The systematic use of fertilizers causes increasing of soil metabolic acidity. The research findings have practical and theoretical significance, providing valuable insights for enhancing agricultural crop productivity through improving soil management in the agroecosystems.

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